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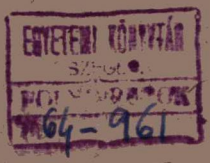

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BÉRCES T., GYULAI J. és HALMOS M.

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INTERNAL STRUCTURE OF PHYSICAL FIELDS

By J. I. HORVÁTH

Institute of Theoretical Physics, József Attila University, Szeged

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The handedness, *i. e.*, the right and left asymmetry of elementary particles is explained in terms of the relativistic phase-space formalism. In this way a new development of our previous theory [2] is suggested. In the following the field equations are derived by variational method, the mass-spectrum of baryons are obtained and NOETHER's theorem is generalized. In fact, the transformations, defined usually in the isobaric spin space, appear as continuous transformations. Finally, the philosophical concept of space-time continuum as well as the interpretation of the method suggested is discussed.

§ 1. *Introduction*

The spin and the linear polarization of elementary particles, as well as their various internal attributes — such as baryon charge, isospin, hypercharge and parity — associated with the abstract concept of isospace (isobaric spin space) and its transformations indicate that there must be some additional intrinsic property of the fields, an additional degree of freedom, which has not been fairly considered in terms of the usual formalism of the theory of elementary particles. *E. g.*, the existence of the spin shows in itself that the point-model of elementary particles associated with the familiar local theory of fields does not provide a complete description of the properties of the particles, since, the rotational axis connected with the spin angular momentum cannot be explained in a natural manner. Furthermore, the linear polarization — *i. e.* the space-independent correlation of the momentum and the spin angular momentum of fermions — proves that this distinguished direction may be in close connection with the anisotropic internal structure of particles not properly considered previously. The intrinsic anisotropy of particles appears first of all in their handedness by which the asymmetry of right and left is expressed. Of course, on the bases of an extended particle-model or based on a rigid-body model this anisotropy could be characterized [1], but the relativistic formulation of such a theory would be rather difficult and the results of such theories would only be cumberously translated into the language of field theories. Moreover, taking the current methods of the theory of elementary particles into account, it can be noticed that these methods have, from certain point of view, two essential different features. Some of them are closely connected with geometry and obtain such physical laws as conservation of energy and momentum, *etc.*; the others, nevertheless, are rather based on the abstract concept of the isospace than current geometrical terms and

result in such physical laws as the conservation of charge or that of baryon number, *etc.* In other words, some of the groups of transformations — like translation, rotations and inversions in the four-dimensional spacetime continuum — possess an immediate geometrical meaning, but some of the others — such as *e. g.* gauge transformation of first kind, charge conjugation, charge-symmetry and mesoparity transformation — possess none. However, the reality of these latter attributes of elementary particles indicate that the angles of isorotations as well as the planes of isoreflexions are not located in an abstract space, but within space-time itself. This is the reason that several investigations have been recently published to explain the internal degrees of freedom of physical fields as well as to interpret the isospace and its transformations in geometrical terms. These proposals are, of course, very different.

Our recent investigations [2] in this direction have been based on the supposition that in the anisotropic internal structure of the elementary particles the anisotropy of the space-time continuum would appear. Having FRÖHLICH's theory in mind [3—5], based on terms of the relativistic phase-space formalism the suggested theory can be developped as follows.

§ 2. *The Relativistic Phase-space and the Internal Structure of Physical Fields*

Let us provisionally suppose that the structure of the space-time continuum is pseudo-EUCLIDIAN, *i. e.*, its metrical fundamental tensor has the components

$$\gamma_{00} = 1, \quad \gamma_{0i} = 0, \quad \gamma_{ik} = -\delta_{ik}, \qquad (i, k = 1, 2, 3) \quad (2,1)$$

where δ_{ik} means the KRONECKER's tensor.

First of all, we would explain the handedness, *i. e.*, the right and left asymmetry of the elementary particles.

In the four-dimensional space-time continuum in a certain LORENTZ frame $\mathfrak{K}$ the particle considered has the position coordinates $\{x^\mu\}$ and the components of its momentum four-vector are $\{p^\mu\}$ $(\mu = 0, 1, 2, 3)$ which fulfil the well-known relation:

$$p^\mu p_\mu = m_0^2 \geqq 0, \qquad (2,2)$$

together with the postulate that this definition should be invariant under continous LORENTZ transformation, where m_0 denotes the rest mass of the particle ($\hbar = c = 1$). Although, the components of the momentum have to fulfil condition (2,2), they are otherwise in all points of the space-time continuum quite arbitrary. Hence, the state of the particles can be easily characterized by introducing in every point $\{x^\mu\}$ of the *co-ordinate-space* a local *momentum-space* $\{p^\mu\}$ wherein the momentum four-vector p^μ can be regarded as radius vector. The position and momentum co-ordinates of the particle, *i. e.*, the rectangular coordinates $\{x^\mu\}$ and $\{p^\mu\}$ altogether determine the so-called *phase-space*, in which an arbitrary point $\{x^\mu, p^\mu\}$ refers to a special state of the particle considered.

Owing to the relation (2,2), however, the components of the momentum four-vector are not independent, namely, by the four numbers $\{p^\mu\} = \{p^0, p^k\}$ the relation

$$(p^0)^2 - \sum_{k=1}^{3} (p^k)^2 = m_0^2 \qquad (2,3)$$

has to be fulfilled. By the notation

$$\sum_{k=1}^{3} (p^k)^2 \equiv p^2 \tag{2,4}$$

one can obtain that

$$p = \pm \{m_0^2 + p^2\}^{1/2}. \tag{2,5}$$

In fact, the local momentum-space has only three independent momentum co-ordinates. This means, of course, that in the co-ordinate-space $\{x^\mu\}$ by the radius vector of the momentum-space, *i. e.* by the four momentum components $\{p^\mu\}$, only a direction is determined. As a matter of fact, the phase-space has $4+3$ dimensions.

In the case of a co-ordinate transformation

$$\bar{x}^\mu = \bar{x}^\mu(x^\mu) \qquad \left(\Delta \equiv \det \left| \frac{\partial \bar{x}^\mu}{\partial x^\mu} \right| \neq 0\right) \tag{2,6}$$

the law of transformation of the momentum is given by

$$\bar{p}^\mu = \frac{\partial \bar{x}^\mu}{\partial x^\varrho} p^\varrho. \tag{2,7}$$

In the following, let us only consider the complete group of LORENTZ transformations which will be denoted by $\mathcal{G}_x$.

A LORENTZ transformation in momentum-space may be interpreted in two ways: either the co-ordinate axes are considered fixed and the radius vector has been changed according to (2,7) [the active interpretation of the group], or *vice versa* [the passive interpretation of the group]. The latter interpretation determines the possible frames of reference in the local momentum-space in terms of the frame $\mathfrak{K}$ originally introduced in the co-ordinate-space $\{x^\mu\}$.

Due to the double sign of p^0 both of the radius vectors $\{p^0, p^k\}$ and $\{-p^0, p^k\}$ fulfil the relations (2,2) and (2,3), respectively. Of course, these radius vectors can be transformed in a continuous way into one an other, or into any radius vector of the momentum-space. Taking the complete group of LORENTZ transformation into account — as FRÖHLICH pointed out in [5] — these transformations may thus be considered as generating two „three-dimensional" momentum-spaces: one with $p^0 > 0$ and the other with $p^0 < 0$.

The frames of reference have certain features that can be chosen arbitrarily; *e. g.*, the frame $\mathfrak{K}$ of the co-ordinate-space may be a right-handed system. In this case — having the sign of p^0 — in the momentum-space only the directions of space axes of the local frame of reference can be chosen arbitrarily. Let us suppose, for instance that its spatial axes form a right-handed system, then the local frame of reference of the momentum-space is right-handed if $p^0 > 0$ and left-handed if $p^0 < 0$.

Considering in the subspace $\{x^k\}$ the inversion in respect to the origin:

$$\bar{x}^0 = x^0, \ \bar{x}^1 = -x^1, \ \bar{x}^2 = -x^2, \ \bar{x}^3 = -x^3 \tag{2,8}$$

the momentum components p^k transform into $-p^k$. This means in terms of the passive interpretation of co-ordinate transformations that we have changed the handedness of the local frame of reference in the momentum-space, *i. e.* a right-

handed frame in $\{p^k\}$ subspace (assuming that the original $\{x^k\}$ frame was right-handed) transforms into a left-handed one. It is obvious that the definitions (2,2) and (2,3) from which the properties of the momentum-space were originally defined do not permit distinction between right-handed and left-handed systems because (2,3) does not contain p^k but only $(p^k)^2$.

Owing to the above considerations to be explicitly expressed on the one hand that the momentum-space is three dimensional and on the other hand that the handedness of the local frame of reference in the momentum-space is arbitrary, let us introduce in the $\{x^\mu\}$ point of the co-ordinate-space three unit vectors λ_i^μ $(i=1, 2, 3)$ which may be, without restriction of generality, by pairs orthogonal, *i. e.*

$$\gamma_{\mu\nu}\lambda_i^\mu\lambda_j^\nu = \delta_{ij}. \tag{2,9}$$

The three degrees of freedom of the momentum-space may be characterized by the angles

$$\vartheta_i = \arccos\{\gamma_{\mu\nu}\lambda_i^\mu p^\nu/m_0\}, \tag{2,10}$$

between the direction corresponding to the radius vector p^μ and the unit vectors λ_i^μ. The angles ϑ_i and the scalar quantities

$$\zeta_i \equiv \cos\vartheta_i = \gamma_{\mu\nu}\lambda_i^\mu p^\nu/m_0 = \lambda_i^\mu p_\mu/m_0, \tag{2,11}$$

respectively, in the case of any fixed direction of the unit vectors λ_i^μ determine unambigously the direction in the co-ordinate-space $\{x^\mu\}$ characterized by the radius vector p^μ. Call the three by pairs orthogonal unit vectors λ_i^μ in the following as λ-trieder. Of course, the λ-trieder as new local frame of reference and the ensemble of the quantities $\{\zeta_i\}$ as independent co-ordinates, or as the independent components of the radius vectors in the momentum-space, can be regarded. Indeed, in this manner any direction in the co-ordinate-space corresponding to the direction determined by the momentum vectors p^μ can unambigously be characterized.

Due to the definition (2,11) of the quantities $\{\zeta_i\}$ one sees immediately that they are invariant under any LORENTZ transformation; *e. g.*, in the case of the inversion (2,8) the quantities ζ_i do not change, since the spatial components of the λ_i^μ and p^μ vectors change their sign simultaneously. Considering this property of the quantities $\{\zeta_i\}$ the doubling of the momentum-space appears again. The inversion (2,8) transforms, namely, the λ-trieder $\{\lambda_i^0, \lambda_i^k\}$ into $\{\lambda_i^0, -\lambda_i^k\}$ and this transformation indicates simultaneously the change of $\{p^0, p^k\}$ into $\{p^0, -p^k\}$. In fact, the inversion (2,8) changes the handedness of the λ-trieder in the spatial subspace of the momentum-space. However, the quantities depend linearly on the base vectors λ_i^μ of the new local frame of reference of the momentum-space, therefore, the sign of the quantities $\{\zeta_i\}$ depends on the handedness of the λ-trieder. For the sake of simplicity denote the λ-trieder with base vectors $\{\lambda_i^0, \lambda_i^k\}$ as λ^+-trieder, and the other with base vectors $\{\lambda_i^0, -\lambda_i^k\}$ as λ^--trieder.

For the sake of appropriateness let the directions of the λ-trieder axes be chosen in a special way. Considering the fact that by the introduction of the local momentum-space those properties of the particles have to be characterized which are independent of their translatory motions, it seems to be suitable for the direction of the trieder axes to take into account the rest frame of reference $\mathfrak{K}^0$ of the particle in which its momentum components are $\{p_{(0)}^\mu\} = \{p_{(0)}^0, 0, 0, 0\}$. As matters stand, $\mathfrak{K}^0$ is distinguished among the other frame of references $\mathfrak{K}$ that the direction of its time

axis is directed into the direction of the momentum of the particle. Let the directions of the new local frame of reference be fixed in the system $\mathfrak{K}^0$ in any way, then the transformations of the LORENTZ group transform the momentum four-vector $p^\mu_{(0)}$ into the different radius vectors of the momentum-space, and, simultaneously, the quantities $\{\zeta_i\}$ run over the values $-1 \leqq \zeta_i \leqq +1$ $(i=1, 2, 3)$.

To express the doubling of the momentum-space more simply, let us suppose that the by pairs orthogonal λ^μ_i unit vectors are orthogonal to the momentum vector of the particles. This means, however, that in the rest frame of reference $\mathfrak{K}^0$ the relations

$$\underset{(0)}{\zeta_i^{(0)}} = \underset{(0)}{\lambda^\mu_i}\, p_{(0)\mu}/m_0 = 0 \qquad (i=1, 2, 3) \qquad (2{,}12)$$

have to be fulfilled. In fact, the components of the λ^μ_i-trieder axes in $\mathfrak{K}^0$ are $\underset{(0)}{\{\lambda^\mu_i\}} = \{0, \vec{\lambda}_i\}$, where $\vec{\lambda}_i = \underset{(0)}{\{\lambda^k_i\}}$ denote the spatial components of the unit vectors $\underset{(0)}{\lambda^\mu_i}$. Due to (2,9), the $\vec{\lambda}_i$ three-vectors are, indeed, by pairs orthogonal, too, otherwise they can be directed in the $\{x^k\}$ subspace arbitrarily. Of course, we will suppose that the direction of the $\vec{\lambda}_i$-vector coincides with that of the i-th axis of $\mathfrak{K}^0$. In terms of the original local frame of reference of the momentum-space this means that its time-axis is determined by the four-vector $p^\mu_{(0)}$ and its spatial axes coincide with the vectors $\vec{\lambda}_i$. But, in this way also the handedness of the local frame of reference is determined: it is right-handed if $p^0_{(0)} > 0$ and left-handed if $p^0_{(0)} < 0$. In the case of $p^0_{(0)} > 0$ and λ^+-trieder or $p^0_{(0)} < 0$ and λ^--trieder the local frame of reference is right-handed, as well as in the case of $p^0_{(0)} < 0$ and λ^+-trieder or $\lambda^0_{(0)} > 0$ and λ^--trieder it is left-handed. This means, indeed, that the doubling of the momentum-space be characterized by the handedness of the λ-trieder itself.

It is obvious that by fixing the trieder axes in $\mathfrak{K}^0$ the λ^μ_i vectors are be unambiguously determined in all frame of reference. This is the reason that for the sake of simplicity our argumentation will be only developped in the $\mathfrak{K}^0$ system — the co-ordinates of which will be denoted instead of $\{x^\mu_{(0)}\}$ by $\{x^\mu\}$ — namely, our results can be transformed into all frames of reference without any difficulty. Let us, however, emphasize again that the system is distinguished by physical terms: it is the rest system of the particle and it can be, *e. g.*, supposed that the $\vec{\lambda}_3$ axis of the λ-trieder coincides with the direction of rotational axis associated with the spin angular momentum of the particle.

Owing to the definition (2,11) of the quantities $\{\zeta_i\}$, the ζ_i-s are dependent on the momentum conponents $\{p^\mu\}$ and on the direction of the λ-trieder. We have emphasized several times that the quantities ζ_i are invariant under any LORENTZ transformation of the group $\mathcal{G}_{Jx}$. However, intrinsic transformations of the local momentum-space can be introduced by changing the directions of the trieder axes which do not induce any change of the $\{x^\mu\}$ coordinates. These transformations, denoted in the following by $\mathcal{G}_{J\zeta}$, may be identified with the intrinsic motions of the particles referring to the internal degrees of freedom of physical fields. Therefore, let the „co-ordinates" $\{\zeta_i\}$ of the local momentum-space be called as *internal co-ordinates* and the „co-ordinates" $\{x^\mu\}$ of the co-ordinate-space as *external co-ordinates* of the physical fields $\psi = \psi(x^\mu, \zeta_i)$.

It is obvious that the group $\mathcal{G}_\zeta$, *i. e.*, the group of internal transformations can be generated by the rotations of the λ-trieder around its origin and by the reflexions in respect of the trieder. Consider, first of all, the rotations of the λ-trieder which can be characterized by the EULERIAN angles $\{\varphi, \psi, \vartheta\}$:

$$\vec{\lambda}_i' = M_i^k \vec{\lambda}_k, \tag{2,13}$$

where the well-known matrixelements $M_i^k = M_i^k(\varphi, \psi, \vartheta)$ fulfil the orthogonality relations

$$M_i^k M_j^k = \delta_{ij} \quad \text{and} \quad M_i^r M_i^s = \delta^{rs}. \tag{2,14}$$

Due to the definition (2, 11) of the internal co-ordinates their transformation law can be obtained as follows:

$$\zeta_i' = \lambda_i'^{\mu} p_\mu / m_0 = M_i^k \lambda_k^\mu p_\mu / m_0 = M_i^k \zeta_k. \tag{2,15}$$

It is obvious that under the rotation (2, 13) the trieder axes remain orthogonal to the momentum four-vector $p^\mu_{(0)}$, therefore the rotations of the $\mathcal{G}_\zeta$ group are identical with the EUCLIDIAN rotations of the three-dimensional space, *i. e.*, they are isomorphic to the rotations of the spatial subspace of the four-dimensional co-ordinate-space which is orthogonal to $p^\mu_{(0)}$. This can be proved as follows: Let us introduce the notation

$$\delta^{ij}\zeta_i\zeta_j = \zeta_1^2 + \zeta_2^2 + \zeta_3^2 \equiv \zeta^2, \tag{2,16}$$

then, due to (2, 15),

$$\zeta'^2 = \delta^{ij}\zeta_i'\zeta_j' = \delta^{ij} M_i^r M_j^s \zeta_r \zeta_s = M_i^r M_i^s \zeta_r \zeta_s = \delta^{rs}\zeta_r\zeta_s = \zeta^2 \tag{2,17}$$

can be obtained, *i. e.*, ζ^2 remains invariant under the rotations (2, 13), which is just the definition of the EUCLIDIAN rotations. In fact, one can establish a mapping of the rotations of $\mathcal{G}_\zeta$ into the motions of the unit sphere in the local momentum-space which has the equation in its parametric form:

$$\begin{aligned} \zeta_1/\zeta &= \sin\vartheta\cos\varphi \\ \zeta_2/\zeta &= \sin\vartheta\sin\varphi \\ \zeta_3/\zeta &= \cos\vartheta \end{aligned} \tag{2, 18}$$

where (ϑ, φ) mean the polar angles in the momentum-space. Furthermore, one can immediately see that the reflexions of the group $\mathcal{G}_\zeta$ are isomorphic to those of the three-dimensional reflexions, therefore, the group $\mathcal{G}_\zeta$ is isomorphic to the three-dimensional rotary-reflexion group.

The intrinsic anisotropy of elementary particles with non-vanishing spin momentum, characterized by the longitudinal polarization of the particle, means in terms of the theory suggested that only those elements of the local momentum-space have to be considered which form a constant angle with the rotational axis associated with the spin of the particles. If we suppose that this rotational axis coincides in the rest system $\mathfrak{K}^\circ$ of the particle with the $\vec{\lambda}_3$ axis of the λ^+-trieder, then the intrinsic anisotropy may be characterized by the relation:

$$\zeta_3 \equiv \cos\vartheta_3 = \lambda_3^\mu p_\mu / m_0 = \text{const.} \tag{2,19}$$

So far the momentum-space was three-dimensional corresponding to the three internal degrees of freedom, but the relation (2,19) reduces the internal degrees of freedom by one and the internal space becomes only two-dimensional. This means that the adequate directions can be characterized by the internal co-ordinates $\{\zeta_1, \zeta_2\}$.

The characterization of the intrinsic anisotropy of the particles is not yet explicitly covariant. However, it can be easily reformulated in such a way that the direction of the distinguished rotational axis mentioned above is rather characterized by the anisotropy of the co-ordinate-space than explicitly by the $\vec{\lambda}_3$ axis of the λ-trieder.

Let the longitudinal polarization of the particle be denoted by $\mathscr{P}$ and consider the surface in the momentum-space in its parametric form

$$\begin{aligned} \zeta_1/\zeta &= (1+\mathscr{P}\cos\vartheta)\sin\vartheta\cos\varphi \\ \zeta_2/\zeta &= (1+\mathscr{P}\cos\vartheta)\sin\vartheta\sin\varphi \\ \zeta_3/\zeta &= (1+\mathscr{P}\cos\vartheta)\cos\vartheta \end{aligned} \tag{2,20}$$

instead of the unit sphere (2,18), the points of which determine the different directions corresponding to the radius vectors of the local momentum-space. It is obvious that (2,20) is an equation of a rotational surface which distinguishes the direction of the λ_3^μ axis of the λ-trieder.

Let the polar angles (ϑ, φ) be eliminated, then with the abbreviation $y^k = \zeta_k/\zeta$ we have instead of (2,20):

$$\{1+\mathscr{P}y^3[(y^1)^2+(y^2)^2+(y^3)^2]^{-1/2}\}^{-2}[(y^1)^2+(y^2)^2+(y^3)^2] = 1. \tag{2,21}$$

Introducing the metrical fundamental tensor

$$g_{ik} = -\delta_{ik}\{1+\mathscr{P}y^3[(y^1)^2+(y^2)^2+(y^3)^2]^{-1/2}\}^{-2} \qquad (i,k=1,2,3) \tag{2,22}$$

in the $\{y^k\}$ space, (2,21) may be written in the form

$$-g_{ik}y^iy^k = 1. \tag{2,23}$$

The surface (2,20) or (2,22) is defined in the momentum-space, *i. e.*, in all points of the co-ordinate-space $\{x^\mu\}$. Therefore, it can also be defined in the following way:

Consider the „unit vectors" l^μ by re-definition of the metrical structure of the co-ordinate-space. Let the components of the new metrical fundamental tensor be given by

$$g_{00}=1,\ g_{0i}=0,\ g_{ik}=-\delta_{ik}\{1+\mathscr{P}y^3[(y^1)^2+(y^2)^2+(y^3)^2]^{-1/2}\}^{-2} \tag{2,24}$$

which depend on the directions determined by the radius vectors in the momentum-space. Then, the unit vectors l^μ directed in the direction of p^μ may be defined as follows:

$$l^\mu = p^\mu/F, \tag{2,25}$$

where

$$F \equiv \{g_{\mu\nu}p^\mu p^\nu\}^{1/2} \tag{2,26}$$

means the new metrical fundamental function of the co-ordinate-space. One can immediately observe that the components $g_{\mu\nu}$, of the new metrical fundamental tensor as well as the new unit vectors l^μ are homogeneous functions of the $\{p^\mu\}$ „direction co-ordinates" of zero order.

The new metrical structure of the co-ordinate-space may be covariantly characterized by the surface:

$$F(x^\mu, l^\mu) = 1 \tag{2,27}$$

which, as the indicatrix of the space, can be regarded. Its explicit form is

$$(l^0)^2 + g_{ik} l^i l^k = 1. \tag{2,28}$$

Denote the co-ordinates of the end-points of l^μ by y^μ, then we have

$$(y^0)^2 + g_{ik} y^i y^k = 1. \tag{2,29}$$

Comparing (2,29) to (2,23) one observes that the surface (2,23) can be deduced from the indicatrix (2,29) by cutting it by the hyper plane

$$y^0 = \sqrt{2}. \tag{2,30}$$

In fact, the intrinsic anisotropy of the co-ordinate-space due to the internal structure of the particles had been experimentally expressed by the longitudinal polarization of the particles, which can be covariantly characterized by the indicatrix (2,29) of the space. This indicatrix distinguishes a direction in the spatial subspace, namely, its rotational axis, and the geometrical and physical quantities defined in the phase-space are dependent on the directions in respect to this distinguished axis. If the longitudinal polarization of the particle vanishes ($\mathscr{P} = 0$), the metrical fundamental tensor (2,24) is reduced to the metrical fundamental tensor of the pseudo-EUCLIDIAN space (2,1), the adequate section of the indicatrix is instead of (2,23) or (2,20) the sphere (2,18) and the phase space is isotropic.

The metrical fundamental tensor plays an important role in the definition of the scalar product of vectors, therefore, in anisotropic spaces not only the length, but also the angle of inclination of vectors depends on the direction. At the definition of the local frame of reference of the momentum-space as well as that of the EUCLIDIAN rotation of the λ-trieder were apparently an important supposition that the trieder axes were orthogonal in EUCLIDIAN sense. Therefore, the problem occurs whether in the case of the new metric (2,24) our previous results concerning the definition of the group $\mathscr{G}_{4\zeta}$ remained unchanged or not? It will, however, be proved that in the case of the metrical fundamental tensor (2,24) the condition of orthogonality (2, 9) remained valid, *i. e.*, if the trieder axes $\vec{\lambda}_i$ and $\vec{\lambda}_j$ were orthogonal in EUCLIDIAN sense, then they remain orthogonal also in the sense of the new metric. But, we have to mention that the length of the vectors will generally be changed.

Owing to the introduction of the new metric, one has to write the orthogonality relations in the form:

$$g_{\mu\nu} \lambda_i^\mu \lambda_j^\nu = 0, \quad \text{if} \quad i \neq j. \tag{2,31}$$

This means in the rest system of the particle ($\mathfrak{K}^\circ$) that

$$g_{rs} \lambda_i^r \lambda_j^s = 0, \quad \text{if} \quad i \neq j, \tag{2,32}$$

where due to (2,24)

$$g_{rs} = -\delta_{rs} m(p). \quad [m(p) \equiv \{1 + \mathscr{P} p^3 [(p^1)^2 + (p^2)^2 + (p^3)^2]^{-1/2}\}^{-2} \neq 0] \tag{2,33}$$

Hence, (2,32) may be written as

$$m(p) \delta_{rs} \lambda_i^r \lambda_j^s = 0, \quad \text{if} \quad i \neq j, \tag{2,34}$$

and, indeed, one immediately observes that the EUCLIDIAN definition of orthogonality remains valid. Nevertheless, the length of the vectors $\vec{\lambda}_i = \{\lambda_k^i\}$ depends on the direction determined by $\{p^\mu\}$ and the vectors with the components

$$\tilde{\lambda}_i^r = \lambda_i^r / \sqrt{m(p)} \qquad (i = 1, 2, 3) \tag{2,35}$$

are the new unit vectors.

Of course, the definition (2,10) or the angles ϑ_i will be changed, too, and their new definition is

$$\theta_i \equiv \arccos \{g_{\mu\nu}(p) \tilde{\lambda}_i^\mu l^\nu\} \tag{2,36}$$

as well as instead of ζ_i we introduce

$$\xi_i \equiv \cos \theta_i = g_{\mu\nu} \lambda_i^\mu l^\nu \tag{2,37}$$

as new internal co-ordinate. The further results discussed above do not formally change, but in reality in the case of non-vanishing longitudinal polarization all geometrical and physical quantities depend on the direction in respect to the distinguished rotational axis corresponding to the spin angular momentum.

The space of co-ordinates $\{x^\mu, p^\mu\}$, *i. e.*, in our previous terms: the phase-space with anisotropic metric, are usually called in geometry as line-element space which is an ensemble of line-elements, or in other words: an ensemble of all directions $\{p^\mu\}$ in the different points of the space $\{x^\mu\}$. The $\{x^\mu\}$ are the position co-ordinates and the $\{p^\mu\}$ the homogeneous direction coordinates of the line-elements. The line-element geometry with the metrical fundamental tensor (2,24) is a special case of the general line-element geometry previously suggested [6—8]. In this case the angles θ_i and the quantities ξ_i as inhomogeneous direction co-ordinates can be regarded.

§ 3. *The Field Equations*

In current field theories the physical fields are characterized by one or several space-time functions: $\psi(x^\mu)$, $\psi_\alpha(x^\mu)$ *etc.* — fulfilling certain partial differential equations, the so called field equations — having definite laws of transformations under the co-ordinate transformations (2,6). Physical field defined in anisotropic spaces are analogously characterized by such quantities fulfilling the field equations, nevertheless, these functions depend on the line-elements $\{x^\mu, p^\mu\}$, *i. e.*, the field components are: $\psi(x^\mu, p^\mu)$, $\psi_\alpha(x^\mu, p^\mu)$ *etc.* being homogeneous functions of zero degree of the direction co-ordinates $\{p^\mu\}$, of course. Instead of the homogeneous direction co-ordinates let us introduce the inhomogeneous direction co-ordinates θ_i or rather the internal co-ordinates ξ_i.

The field components have to satisfy definite laws of transformations again, however, in this case their characters of transformation are doubled. They have

definite laws of transformation under the transformations of the group $\mathcal{G}_x$ as well as those under the transformations of the group $\mathcal{G}_\xi$. These two kinds of transformation laws are independent. This point will be discussed in the following in details (§ 7.).

Suppose that the LAGRANGIAN of the field depends on the metrical fundamental tensor, on the field components and on their derivatives. For the sake of appropriateness, the symbols:

$$\psi_{\alpha,\mu} \equiv \partial_\mu \psi_\alpha \equiv \frac{\partial \psi_\alpha}{\partial x^\mu} \quad \text{and} \quad \psi_{\alpha|i} \equiv \partial_i^* \psi_\alpha \equiv \frac{\partial \psi_\alpha}{\partial \xi_i} \tag{3,1}$$

will be introduced. Then, the LAGRANGIAN can be implicitly written as follows:

$$\mathfrak{L} = |g|^{-1/2} |\gamma|^{-1/2} L(\psi_\alpha, \psi_{\alpha,\mu}, \ldots, \psi_{\alpha|i}, \ldots), \tag{3,2}$$

where g denotes the determinant of the metrical fundamental tensor of the external space:

$$g \equiv \det |g_{\mu\nu}| \tag{3,3}$$

and γ denotes that of the internal space:

$$\gamma \equiv \det |\gamma_{ik}|, \tag{3,4}$$

the latter with the law of transformation

$$\tilde{\gamma}_{ik} = \frac{\partial \tilde{\xi}_i}{\partial \xi_r} \frac{\partial \tilde{\xi}_k}{\partial \xi_s} \gamma_{rs}, \tag{3,5}$$

where

$$\tilde{\xi}_i = \tilde{\xi}_i(\xi_r) \qquad \left(\Delta^* \equiv \det \left| \frac{\partial \tilde{\xi}_i}{\partial \xi_r} \right| \neq 0 \right) \tag{3,6}$$

means the transformations of the internal space being elements of the group $\mathcal{G}_\xi$. From a geometrical point of view we have, of course, no *a priori* restrictions for the structure of the internal space and its structure may be determined by physical factors. It seems, however, that it can provisionally be assumed that the metrical structure of the internal space is EUCLIDIAN, *i. e.*,

$$\gamma_{ik} = \delta_{ik}. \tag{3,7}$$

Owing to these considerations the integral of action can be written in the form:

$$\mathfrak{J} = \int_\Omega \int_{\Omega^*} \mathfrak{L} \, d^4x \, d^i\xi, \tag{3,8}$$

where $d^i\xi$ means the two-, or three-dimensional volume element of the internal space according to its dimension. The domain of integration for the external co-ordinates is a four-dimensional domain Ω, and for the internal co-ordinates Ω^* with the restriction $-1 \leqq \xi_i \leqq +1$ $(i = 1, 2, 3)$.

The integral of action (3,7) has to be invariant under any transformation of the external and internal space, respectively; *i. e.*, it is an invariant of the general group of transformations

$$\mathcal{G} = \mathcal{G}_x \times \mathcal{G}_\xi. \tag{3,9}$$

In respect to the derivation of the field equations be only mentioned that the variation of $\mathfrak{L}$ has to vanish:

$$\delta\mathfrak{J} = \int_{\Omega}\int_{\Omega^*} \sum_{\alpha} \left\{ \frac{\partial \mathfrak{L}}{\partial \psi_\alpha} \delta\psi_\alpha + \frac{\partial \mathfrak{L}}{\partial \psi_{\alpha,\mu}} \delta\psi_{\alpha,\mu} + \ldots + \frac{\partial \mathfrak{L}}{\partial \psi_{\alpha|i}} \delta\psi_{\alpha|i} \ldots \right\} d^4x\, d^i\xi = 0. \quad (3,10)$$

In fact, as usual $\delta\psi_\alpha$ has to vanish at the limit of the integration domains, therefore, by partial integration

$$\int_{\Omega}\int_{\Omega^*} \sum_{\alpha} \left\{ \frac{\partial \mathfrak{L}}{\partial \psi_\alpha} - \partial_\mu \frac{\partial \mathfrak{L}}{\partial \psi_{\alpha,\mu}} - \ldots - \partial_i^* \frac{\partial \mathfrak{L}}{\partial \psi_{\alpha|i}} - \ldots \right\} \delta\psi_\alpha\, d^4x\, d^i\xi = 0 \quad (3,11)$$

can be obtained for all variation of the field components $\delta\psi_\alpha$, and, finally, we get the field equations:

$$\frac{\partial \mathfrak{L}}{\partial \psi_\alpha} - \partial_\mu \frac{\partial \mathfrak{L}}{\partial \psi_{\alpha,\mu}} - \ldots - \partial_i^* \frac{\partial \mathfrak{L}}{\partial \psi_{\alpha|i}} - \ldots = 0. \quad (3,12)$$

For the sake of simplicity it has been considered a LAGRANGIAN depending only on the first derivatives of the field components. The general cases were previously discussed in details [6—8].

§ 4. *The Mass-spectrum of Fermions*

In order to apply the theory in a particular case, consider the two-component fermion fields investigated by FEYNMAN [9], GELLMANN [10] and MARX [11]; *i. e.*, let us suppose that the LAGRANGIAN has the following explicit form:

$$\mathfrak{L} = -|g|^{-1/2}|\gamma|^{-1/2} \sum_{A} g^{\mu\nu}\partial_\mu \overline{\psi}_A \partial_\nu \psi_A + \gamma^{ik}\partial_i^* \overline{\psi}_A \partial_k^* \psi_A + \varepsilon \overline{\psi}_A \psi_A\}, \quad (4,1)$$

where the index A distinguishes the two components of the fermion field corresponding to different spin states ($A = \uparrow, \downarrow$). Substituting this LAGRANGIAN into the integral of action by variation in respect to ψ_A the field equations

$$\partial^\mu \partial_\mu \psi_A + \partial^{*i}\partial_i^* \psi_A - \varepsilon\psi_A = 0 \quad (4,2)$$

can be obtained, where

$$\partial^\mu \equiv g^{\mu\nu}\partial_\nu \quad \text{and} \quad \partial^{*i} \equiv \gamma^{ik}\partial_k^*. \quad (4,3)$$

As a matter of fact, if we suppose that

$$\psi_A(x^\mu, \xi_i) = X_A(x^\mu)\Xi_A(\xi_i) \quad (4,4)$$

Eq. (4, 2) can be separated:

$$X_A^{-1}\{\partial^\mu \partial_\mu X_A\} = -\Xi^{-1}\{\partial^{*i}\partial_i^* \Xi_A - \varepsilon\Xi_A\}, \quad (4,5)$$

and, finally, if the constant of separation is denoted by $\varkappa^2$ we have

$$\begin{aligned} &\{\partial^\mu \partial_\mu - \varkappa^2\} X_A = 0, \\ &\{\partial^{*i}\partial_i^* + (\varkappa^2 - \varepsilon)\}\Xi_A = 0. \end{aligned} \quad (4,6)$$

One can immediately observe that the result obtained is very analogous to that derived previously in the case of bilocal theory of fields reformulated it in terms of the general line-element geometry [6—8].

The second equation of (4,6) is the well-known differential equation of an eigenvalue problem for the constant of separation $\varkappa^2$, the spectrum of which — taking into account its meaning in the first equation of (4,6) — gets the mass-spectrum of fermions under consideration ($\hbar = c = 1$).

The internal space has in the case of fermions two dimensions, so that the eigenvalue problem corresponding to the second equation of (4,6) can explicitly be written as follows:

$$\{\partial_1^{*2} + \partial_2^{*2} + (\varkappa^2 - \varepsilon)\}\Xi_A = 0. \tag{4,7}$$

This equation is, indeed, the differential equation of the eigenvalue problem of the two-dimensional rotator.

In terms of polar co-ordinates

$$\xi_1 = r\cos\varphi, \quad \xi_2 = r\sin\varphi \qquad (r = \sqrt{2J} = \text{const}). \tag{4,8}$$

Eq. (4,7) can be written into the form

$$\left\{\frac{1}{2J}\frac{d^2}{d\varphi^2} + (\varkappa^2 - \varepsilon)\right\}\Xi_A = 0, \tag{4,9}$$

where J means the moment of inertia. Considering, of course, the usual condition of periodicity $0 \leqq \varphi \leqq 2\pi$, the following eigenvalues and eigenfunctions can be obtained:

$$\varkappa_n^2 = \varepsilon + \frac{1}{2J}n^2 \qquad (n = 0, \pm 1, \pm 2, \ldots) \tag{4,10}$$

$$\Xi_A^{(n)} = \frac{1}{\sqrt{2\pi}}\exp\{in\varphi\}. \tag{4,11}$$

The case $n = 0$ has to be excluded, namely for $n = 0$ the eigenfunction $\Xi_A^{(0)}$ would not depend on the internal co-ordinates which is in contradiction with the general supposition that all physical quantities have to depend on the internal co-ordinates, too. In fact, to express this circumstance explicitly, let the notation

$$n = S + 1 \qquad (S = 0,1,2, \ldots) \tag{4,12}$$

be introduced.

Unfortunately, in the expression (4,10) of $\varkappa_S^2$ the constant ε and J are unknown and we have not yet any possibility to get their *a priori* values which would only be expected in the frame of a non-linear theory where also the interactions of fields are taken into account. Nevertheless, one can immediately observe that for $\varkappa_S^2$ in the case $S \geqq 2$ the relation

$$\varkappa_3^2 = \varkappa_0^2 + \frac{1}{3}\{(S+1)^2 - 1\}[\varkappa_1^2 - \varkappa_0^2] \tag{4,13}$$

can be obtained. In fact, for a family of particles if the masses of the first two isodoublets are known, the masses of the heavier isodoublets can be calculated by means of (4,13). This is the case for baryons as it will be shown in the next paragraph.

§ 5. *The Mass-spectrum of Baryons*

Owing to our previous result reviewed in § 4. of this paper, the fermions form isodoublets. In fact, this result does not agree with the usual supposition according to which the Σ hyperons form an isotriplet and Λ° particle is an isosinglet. It is, however, in full agreement with the hypothesis of the global baryon-pion interaction suggested by GELL-MANN [12]. In formulating this principle, one has to consider that the pion interaction of hyperons of first order ($\Lambda^\circ, \Sigma^+, \Sigma^\circ, \Sigma^-$) shows threedimensional isotropic invariance both if the four particles are divided into two doublets as well as if they form a singlet and triplet. This remarkable fact has been emphasized also by SCHWINGER [13] who at the same time proposed a possible explanation in the frame of the four-dimensional isospace. In order to overcome the difficulty of SCHWINGER's scheme that in the case of baryons of even order (p, n, Ξ°, Ξ^-) an other subgroup of the six-parametric symmetry group must be identified with the three-dimensional symmetry group of kaons as in the case of baryons of odd order ($\Lambda^\circ, \Sigma^+, \Sigma^\circ, \Sigma^-$), GELL-MANN's idea has been more recently reinvestigated by KÁROLYHÁZY and MARX [14] whose theory reproduces the important results of GELL-MANN, SCHWINGER and others, but, is free from this difficulty.

The theory of KÁROLYHÁZY and MARX has been built up on a four-dimesional mathematical scheme proposed for particles being in strong interactions with each other. To describe the pions and the nucleons they need three and two independent components, respectively; therefore, the former are represented by the spinor $\pi_\mu{}^\nu = \pi_\nu{}^\mu$ and the latter by a spinor B_α. For the description of the hyperons of first order ($\Lambda^\circ, \Sigma^+, \Sigma^\circ, \Sigma^-$) a spinor $B_{\alpha\dot{\nu}}$ was suggested. In fact, pions and nucleons have nothing to do with dotted indices, hence, it can be supposed that the number of dotted indices is related to the absolute values of the strangeness. This means, however, that the doublet of kaons is represented by the spinor $K_{\dot{\mu}}$, furthermore, the baryons are described by spinors with one undotted and so many dotted indices as is the order (*i. e.*, absolute value of the strangeness) of the baryon which brings KRÓLIKOWSKY's theory in mind:

$$\begin{aligned} &|S|=0 : B_\alpha \quad : p, n \\ &|S|=1 : B_{\alpha\dot{\sigma}} \; : \Lambda^\circ, \Sigma^+, \Sigma^\circ, \Sigma^- \\ &|S|=2 : B_{\alpha\dot{\sigma}\dot{\tau}} : \Xi^\circ, \Xi^-, \Omega^+, \Omega^\circ, \Omega^-, \Omega^{--} \\ &\quad\cdots \qquad \cdots \qquad \cdots \end{aligned} \tag{5,1}$$

As a matter of fact, the baryons are split into doublets:

$$\begin{pmatrix} B_1 \\ B_2 \end{pmatrix} = \begin{pmatrix} p \\ n \end{pmatrix}; \begin{pmatrix} B_{1\dot{1}} \\ B_{1\dot{2}} \end{pmatrix} = \begin{pmatrix} \Sigma^+ \\ 1/\sqrt{2}(\Lambda^0 - \Sigma^0) \end{pmatrix}; \begin{pmatrix} B_{2\dot{1}} \\ B_{2\dot{2}} \end{pmatrix} = \begin{pmatrix} 1/\sqrt{2}(\Lambda^0 + \Sigma^0) \\ \Sigma^- \end{pmatrix}; \ldots \textit{ etc.} \tag{5,2}$$

Antibaryons are represented by the complex conjugate of the corresponding spinors, B_α^*, *etc.*

Bearing the classification (5, 1) of baryons in mind, one observes that *the quantum number S of our isorotator introduced in the last paragraph as the absolute value of the strangeness can be interpreted and the exitation of the isorotator* $n = S + 1$ *agrees with the number of isodoublets of type* (5,2). Furthermore, one can observe that due to the double sign of the quantum number n in Eq. (4,10) and (4,11),

respectively, $\pm(|n|-1)$ — with $n \neq 0$ — immediately with the strangeness of the particles can be identified, and the double degeneracy of isorotator states may be associated with the well-known property of the scheme of GELL-MANN—NISHIJIMA that the strangeness of baryons and antibaryons have opposite signs.

So far, as only pion-interactions are considered, the masses of the different isodoublets are the same and the mass-spectrum of baryons can be described by the relation (4,13). As a matter of fact, let us suppose that $\varkappa_0^2$ and $\varkappa_1^2$ equal with the averages of the masses of nucleons and of that of the hyperons of first order [15], then due to Eq. (4,13) the mass-average of the hyperons of second order can be obtained. Our calculations are summarized in Table I. (the unit of mass is the mass of electrons). In fact, the agreement is satisfactory. The calculated average

Table I.

Elementary particle	Observed mass	Mass-average	
		observed	calculated
p	$1836{,}03 \pm 0{,}02$	1837	—
n	$1938{,}56 \pm 0{,}02$		
Λ^0	$2182{,}39 \pm 0{,}24$	2295	—
Σ^+	$2327{,}4 \pm 0{,}69$		
Σ^0	$2329\ {}^{+1{,}8}_{-3{,}7}$		
Σ^-	2342 ± 1		
Ξ^0	2585 ± 1	2590	2901,92
Ξ^-	2595 ± 39		

value of the mass of hyperons of second order differs by 12% from that of xions. As matters stand, this difference may be reasonable, namely, the mass-average of these hyperons must be somewhat larger than the mass-avarege of xions expected. Indeed, in calculating the mass-average of the hyperons of second order — mentioned as the observed mass-average of xions in Table I. — the masses of the hypothetical Ω particles could not be considered.

The splitting of the degenerate baryon states into isomultiplets will be performed first of all by kaon interactions ($\Lambda - \Sigma$ mass-splitting). Electromagnetic interactions will go a step further and distinguish the $\vec{\lambda}_3$ axis of the λ-trieder and it remains only the invariance with respect to the rotations about this axis. Indeed, the electromagnetic interactions cause further mass-splitting: $p-n$, $\Sigma^+ - \Sigma$, $\Xi^\circ - \Xi^-$, *etc.*

The Ω particles are hypothetical ones, the mass of which is about the sum of the xion- and pion-mass. If actual, the $\Omega - \Sigma$ mass difference is larger than the Ξ mass, then the Ω-hyperons decay in a very short time (about 10^{-22} sec) into xions, and is practically unobservable. Nevertheless, it cannot be omitted from our scheme, as the Σ° hyperon — having a lifetime longer by only a few orders — plays also decisive role.

Of course, it is an interesting problem whether the other isodoublets suggested for $S \geqq 2$ by the formula (5,13) will be observed in the future or not.

In order to find also the fine structure of the mass-spectrum, one has to consider the interactions of fields, too. However, this will be discussed in the future.

§ 6. *Mass-spectrum in the Case of Three-dimensional Isospace*

In the case of three-dimensional internal space the second equation of (4,6) has the explicit form:

$$\{\partial_1^{*2} + \partial_2^{*2} + \partial_3^{*2} + (\varkappa^2 - \varepsilon)\}\Xi = 0. \tag{6,1}$$

This is the differential equation of a three-dimensional rotator. By introducing the polar co-ordinates

$$\xi_1 = \xi \sin\vartheta\cos\varphi,\ \xi_2 = \xi\sin\vartheta\sin\varphi,\ \xi_3 = \xi\cos\vartheta \quad (\xi = \{\xi_1^2 + \xi_2^2 + \xi_3^2\}^{1/2} = \sqrt{2M}) \tag{6,2}$$

we have

$$\left\{\frac{1}{2M}\left[\frac{1}{\sin\vartheta}\frac{\partial}{\partial\vartheta}\left(\sin\vartheta\frac{\partial}{\partial\vartheta}\right) + \frac{1}{\sin^2\vartheta}\frac{\partial^2}{\partial\varphi^2}\right] + (\varkappa^2 - \varepsilon)\right\}\Xi(\vartheta, \varphi) = 0. \tag{6,3}$$

Considering those solutions $\Xi(\vartheta, \varphi)$ which are finite, continuous and monovalent in the domains $0 \leqq \vartheta \leqq \pi$ and $0 \leqq \varphi \leqq 2\pi$, they are

$$\Xi^{(l,m)}(\vartheta, \varphi) = Y_{lm}(\vartheta, \varphi), \qquad (l = 0, 1, 2, \ldots\ m = 0, \pm 1, \pm 2, \ldots \pm l) \tag{6,4}$$

where $Y_{lm}(\vartheta, \varphi)$ mean the spherical functions corresponding to the eigenvalues

$$\varkappa_l^2 = \varepsilon + \frac{1}{2M} l(l+1). \tag{6,5}$$

The case $l = 0$ has to be excluded again, namely, $\Xi^{(0,0)} = \text{const.}$ would be in contradiction to our fundamental supposition that Ξ has to depend on the internal coordinates.

So far, the mass-spectrum (6,5) cannot be discussed as well as the constant ε and M cannot be determined in this case, namely, isotriplets with strangeness $|S| > 1$ and with vanishing spin are unknown. However one has to conclude that such particles are possible in this approximation. Considering the interactions of the fields may be motivated while these particles have such a short life time that they are unobservable.

§ 7. *The Generalization of* NOETHER*'s Theorem*

In fact, the field components depend on the external and internal co-ordinates: $\psi_\alpha = \psi_\alpha(x^\mu, \xi_i)$. Investigate how in this case NOETHER's theorem has to be generalized.

Consider any infinitesimal variation of the co-ordinates:

$$\bar{x}^\mu = x^\mu + \delta x^\mu \quad \text{and} \quad \tilde{\xi}_i = \xi_i + \delta^*\xi_i. \tag{7,1}$$

As matters stand, the internal co-ordinates $\{\xi_i\}$ are invariant under any change of the external co-ordinates $\{x^\mu\}$ so that $\delta^*\xi_i$ is induced by the change of the direction of the λ-trieder which involves no change of the external co-ordinates. This

means that δx^μ and $\delta^* \xi_i$ are independent. Denoting the variation of the field component ψ_α induced by δx^μ by $\bar{\psi}_\alpha$, and that induced by $\delta^* \xi_i$ by $\tilde{\psi}_\alpha$, the total variation of ψ_α is defined as

$$\delta \psi_\alpha \overset{\text{def}}{=} \bar{\tilde{\psi}}_\alpha(\bar{x^\mu}, \tilde{\xi}_i) - \psi_\alpha(x^\mu, \xi_i). \tag{7,2}$$

The transformations (7,1) are elements of the group $\mathcal{G}$ defined by $\mathcal{G} = \mathcal{G}_x \cdot \mathcal{G}_\xi$.

The local variation of the field components ψ_α may be defined as follows:

$$\delta^0 \psi_\alpha \overset{\text{def}}{=} \tilde{\bar{\psi}}_\alpha(x^\mu, \xi_i) - \psi_\alpha(x^\mu, \xi_i). \tag{7,3}$$

This means, however, in first order of δx^μ and $\delta^* \xi_i$ that

$$\delta \psi_\alpha = \delta^0 \psi_\alpha + \tilde{\bar{\psi}}_\alpha(x^\varrho + \delta x^\varrho, \xi_r + \delta^* \xi_r) - \tilde{\bar{\psi}}_\alpha(x^\varrho, \xi_r) = \delta^0 \psi_\alpha + \psi_{\alpha,\varrho} \delta x^\varrho + \psi_{\alpha|r} \delta^* \xi_r. \tag{7,4}$$

The total variation of ψ_α does not commute with the derivation according to the co-ordinates, nevertheless, the local variation does. Otherwise, we have:

$$\delta \psi_{\alpha,\mu} = \partial_\mu \delta^0 \psi_\alpha + \psi_{\alpha,\mu\varrho} \delta x^\varrho + \psi_{\alpha,\mu|r} \delta^* \xi_r = \partial_\mu \delta \psi_\alpha - \psi_{\alpha,\varrho} \partial_\mu \delta x^\varrho, \tag{7,5}$$

$$\delta \psi_{\alpha|i} = \partial_i^* \delta^0 \psi_\alpha + \psi_{\alpha,\varrho|i} \delta x^\varrho + \psi_{\alpha|ir} \delta^* \xi_r = \partial_i^* \delta \psi_\alpha - \psi_{\alpha|r} \partial_i^* \delta^* \xi_r. \tag{7,6}$$

The total variation of the integral of action — being an invariant of the group $\mathcal{G}$ — has to vanish under the transformations (7,1)

$$\begin{aligned} \delta \mathfrak{J} = & \int_{\bar{\Omega}} \int_{\tilde{\Omega}^*} \tilde{\bar{L}}[\tilde{\bar{\psi}}_\alpha(\bar{x^\mu}, \tilde{\zeta}_i), \tilde{\bar{\psi}}_{\alpha,\mu}(\bar{x^\mu}, \tilde{\xi}_i), \tilde{\bar{\psi}}_{\alpha|i}(\bar{x^\mu}, \tilde{\xi}_i)]\, d^4 \bar{x}\, d^i \tilde{\xi} - \\ & - \int_{\Omega} \int_{\Omega^*} L[\psi_\alpha(x^\mu, \xi_i), \psi_{\alpha,\mu}(x^\mu, \xi_i), \psi_{\alpha|i}(x^\mu, \xi_i)]\, d^4 x\, d^i \xi = 0, \end{aligned} \tag{7,7}$$

where we have implicitly supposed that the metrical fundamental tensors of the external and internal spaces remain unchanged as well as we considered that $|g| = |\gamma| = 1$. The general case was previously investigated in details in [7]. $\delta \mathfrak{J}$ may, however, be written in the form:

$$\begin{aligned} \delta \mathfrak{J} = & \int_{\Omega} \int_{\Omega^*} \delta^0 L d^4 x d^i \xi + \int_{\bar{\Omega}} \int_{\tilde{\Omega}^*} L(\tilde{\bar{\psi}}_\alpha, \tilde{\bar{\psi}}_{\alpha,\mu}, \tilde{\bar{\psi}}_{\alpha|i})\, d^4 \bar{x}\, d^i \tilde{\xi} - \\ & - \int_{\Omega} \int_{\Omega^*} L(\psi_\alpha, \psi_{\alpha,\mu}, \psi_{\alpha|i}) d^4 x\, d^i \xi. \end{aligned} \tag{7,8}$$

Supposing that the LAGRANGIAN L is form invariant, the local variation $\delta^\circ L$ vanishes and we have

$$\delta \mathfrak{J} = \int_{\bar{\Omega}} \int_{\tilde{\Omega}^*} L(\tilde{\bar{\psi}}_\alpha, \tilde{\bar{\psi}}_{\alpha,\mu}, \tilde{\bar{\psi}}_{\alpha|i}) d^4 \bar{x}\, d^i \tilde{\xi} - \int_{\Omega} \int_{\Omega^*} L(\psi_\alpha, \psi_{\alpha,\mu}, \psi_{\alpha|i}) d^4 x\, d^i \xi. \tag{7,9}$$

The form invariance of the LAGRANGIAN is defined by several authors directly by this equation [15].

Owing to (7,2) — due to (7,5) and (7,6) — we have

$$L(\tilde{\bar{\psi}}_\alpha, \tilde{\bar{\psi}}_{\alpha,\mu}, \tilde{\bar{\psi}}_{\alpha|i}) = L(\psi_\alpha + \delta\psi_\alpha, \psi_{\alpha,\mu} + \delta\psi_{\alpha,\mu}, \psi_{\alpha|i} + \delta\psi_{\alpha|i}) =$$

$$= L(\psi_\alpha, \psi_{\alpha,\mu}, \psi_{\alpha|i}) + \frac{\partial L}{\partial \psi_\alpha}\delta\psi_\alpha + \frac{\partial L}{\partial \psi_{\alpha,\mu}}\delta\psi_{\alpha,\mu} + \frac{\partial L}{\partial \psi_{\alpha|i}}\delta\psi_{\alpha|i} = \tag{7,10}$$

$$= L + \frac{\partial L}{\partial \psi_\alpha} + \frac{\partial L}{\partial \psi_{\alpha,\mu}}\partial_\mu\delta\psi_\alpha - \frac{\partial L}{\partial \psi_{\alpha,\mu}}\psi_{\alpha,\varrho}\partial_\mu\delta x^\varrho +$$

$$+ \frac{\partial L}{\partial \psi_{\alpha|i}}\partial_i^*\delta\psi_\alpha - \frac{\partial L}{\partial \psi_{\alpha|i}}\psi_{\alpha|r}\partial_i^*\delta^*\xi_r.$$

Considering

$$\partial_\mu\left(\frac{\partial L}{\partial \psi_{\alpha,\mu}}\delta\psi_\alpha\right) = \partial_\mu\left(\frac{\partial L}{\partial \psi_{\alpha,\mu}}\right)\delta\psi_\alpha + \frac{\partial L}{\partial \psi_{\alpha,\mu}}\partial_\mu\psi_\alpha, \text{ etc.}, \tag{7,11}$$

one gets

$$L(\tilde{\bar{\psi}}_\alpha, \tilde{\bar{\psi}}_{\alpha,\mu}, \tilde{\bar{\psi}}_{\alpha|i}) = L + \left[\frac{\partial L}{\partial \psi_\alpha} - \partial_\mu\frac{\partial L}{\partial \psi_{\alpha,\mu}} - \partial_i^*\frac{\partial L}{\partial \psi_{\alpha|i}}\right]\delta\psi_\alpha +$$

$$+ \partial_\mu\left(\frac{\partial L}{\partial \psi_\alpha} - \frac{\partial L}{\partial \psi_{\alpha,\mu}}\psi_{\alpha,\varrho}\delta x^\varrho\right) + \partial_\mu\left(\frac{\partial L}{\partial \psi_{\alpha,\mu}}\psi_{\alpha,\varrho}\right)\delta x^\varrho + \tag{7,12}$$

$$+ \partial_i^*\left(\frac{\partial L}{\partial \psi_\alpha} - \frac{\partial L}{\partial \psi_{\alpha|i}}\psi_{\alpha|r}\delta^*\xi_r\right) + \partial_i^*\left(\frac{\partial L}{\partial \psi_{\alpha|i}}\psi_{\alpha|r}\right)\delta^*\xi_r.$$

The JACOBIANS of the transformations (2,6) and (3,6) in the case of the infinitesimal transformations (7,1) in first order of δx^μ and $\delta^*\xi_i$ have the explicit form:

$$\Delta = 1 + \partial_\varrho\delta x^\varrho \quad \text{and} \quad \Delta^* = 1 + \partial_r^*\delta^*\xi_r, \tag{7,13}$$

respectively. This means, however, that

$$\delta\mathfrak{J} = \int_\Omega \int_{\Omega^*} \{L(\psi_\alpha + \delta\psi_\alpha, \psi_{\alpha,\mu} + \delta\psi_{\alpha,\mu}, \psi_{\alpha|i} + \delta\psi_{\alpha|i})(1 + \partial_\varrho\delta x^\varrho)(1 - \partial_r^*\delta^*\xi_r) - \tag{7,14}$$

$$- L(\psi_\alpha, \psi_{\alpha,\mu}, \psi_{\alpha|i})\}\, d^4x\, d^i\xi.$$

Taking into account that

$$\partial_\varrho L = \frac{\partial L}{\partial x^\varrho} + \frac{\partial L}{\partial \psi_\alpha}\psi_{\alpha,\varrho} + \frac{\partial L}{\partial \psi_{\alpha,\mu}}\psi_{\alpha,\mu\varrho} + \frac{\partial L}{\partial \psi_{\alpha|i}}\psi_{\alpha,\varrho|i}, \text{ etc.}, \tag{7,15}$$

furthermore, that δx^μ are independent of ξ_i and $\delta^*\xi_r$ are independent of x^μ, respectively, it can, finally, be obtained by simple calculations that

$$\delta\mathfrak{J} = \int_\Omega \int_{\Omega^*} \{\partial_\mu \mathfrak{f}^\mu + \partial_i^* \mathfrak{f}^{*i}\}\, d^4x\, d^i\xi = 0 \tag{7,16}$$

where the abbreviations are introduced:

$$\mathfrak{f}^{\mu} \overset{\text{def}}{=} \left(L\delta^{\mu}_{\varrho} - \frac{\partial L}{\partial \psi_{\alpha,\mu}} \psi_{\alpha,\varrho} \right) \delta x^{\varrho} - \frac{\partial L}{\partial \psi_{\alpha,\mu}} \psi_{\alpha|r} \delta^{*} \xi_{r} + \frac{\partial L}{\partial \psi_{\alpha,\mu}} \delta \psi_{\alpha}; \tag{7,17}$$

$$\mathfrak{f}^{*i} \overset{\text{def}}{=} \left(L\delta^{i}_{r} - \frac{\partial L}{\partial \psi_{\alpha|i}} \psi_{\alpha,r} \right) \delta^{*} \xi_{r} - \frac{\partial L}{\partial \psi_{\alpha|i}} \psi_{\alpha,\varrho} \delta x^{\varrho} + \frac{\partial L}{\partial \psi_{\alpha|i}} \delta \psi_{\alpha}. \tag{7,18}$$

In fact, the integration domains Ω and Ω^{*}, respectively, — the latter within the unit sphere of the $\{\xi_i\}$ space — are arbitrary, so that due to (7,16) the generalization of the contonuity equation:

$$\partial_{\mu} \mathfrak{f}^{\mu} + \partial^{*}_{i} \mathfrak{f}^{*i} = 0 \tag{7,19}$$

can be obtained. Denoting by $\vec{\mathfrak{f}} = \{\mathfrak{f}^{k}\}$ and by $\vec{\mathfrak{f}}^{*} = \{\mathfrak{f}^{*k}\}$, respectively, the spatial components of $\mathfrak{f}^{\mu}$ and $\mathfrak{f}^{*k}$, as well as by $\vec{\nabla}_{(x)} = \{\partial_k\}$ and by $\vec{\nabla}_{(\xi)} = \{\partial^{*}_{k}\}$ the corresponding nabla operators, then (7,19) can be written in the form:

$$\partial_0 \mathfrak{f}^0 + \vec{\nabla}_{(x)} \vec{\mathfrak{f}} + \vec{\nabla}_{(\xi)} \vec{\mathfrak{f}}^{*} = 0. \tag{7,20}$$

Let V be the projection of Ω onto the spatial part $\{x^{\mu}\}$ of the co-ordinate space, surrounded by the closed surface F, then due to GAUSS' theorem

$$\int_{V} \partial_k \mathfrak{f}^k \, d^3x = \int_{V} \vec{\nabla}_{(x)} \vec{\mathfrak{f}} \, d^3x = \oint_{F} \mathfrak{f}^k n_k \, df \tag{7,21}$$

can be obtained where $\{n_k\}$ means the unit normal vector of the surface element df of F. At the spatial limit $F \to \infty$ this integral vanishes, if one supposes — as it is usual — that the field components and their derivatives vanish at the infinity.

The integral in the internal space may analogously be transformed. Now, let Ω^{*} be in this case the internal part of the unit sphere Γ^{*} in the internal space, then due to GAUSS' theorem we have again:

$$\int_{\Omega^{*}} \partial^{*}_{k} \mathfrak{f}^{*k} \, d^i\xi = \int_{\Omega^{*}} \vec{\nabla}_{(\xi)} \vec{\mathfrak{f}}^{*} \, d^i\xi = \oint_{\Gamma^{*}} \mathfrak{f}^{*k} n^{*}_{k} \, d\Gamma^{*} \tag{7,22}$$

where $\{n^{*}_{k}\}$ means the unit normal vector of the surface element $d\Gamma^{*}$ of Γ^{*}. This integral vanishes too, namely, the internal part $\Xi(\xi_i)$ of the field components introduced in Eq. (4,4) is periodical on Γ^{*}.

Introducing the quantity

$$\mathscr{F}^0 \overset{\text{def}}{=} \int_{V} \int_{\Omega^{*}} \mathfrak{f}^0 \, d^3x \, d^i\xi =$$

$$= \int_{V} \int_{\Omega^{*}} \left\{ \left(L\delta^{0}_{\varrho} - \frac{\partial L}{\partial \psi_{\alpha,0}} \psi_{\alpha,\varrho} \right) \delta x^{\varrho} - \frac{\partial L}{\partial \psi_{\alpha,0}} \psi_{\alpha|r} \delta^{*} \xi_{r} + \frac{\partial L}{\partial \psi_{\alpha,0}} \delta \psi_{\alpha} \right\} d^3x \, d^i\xi, \tag{7,23}$$

due to the above considerations, the conservation rule associated with the continuity equation (7,19) can be written in its integral form:

$$\frac{d}{dt} \mathscr{F}^0 = 0, \tag{7,24}$$

i. e., $\mathscr{F}^0$ is a constant of motion.

Summing up, we arrived, at the following important result: any continuous symmetry group induces a conservation law for a certain physical quantity $\mathscr{F}^\circ$ which can be derived for any given system according to (7,23), once the LAGRANGIAN is known. Since, the LAGRANGIANS of the fields are bilinear in the field components ψ_α and their derivatives, the same will hold for the constants of motion belonging to free fields.

The connection between continuous symmetry groups and conservation laws was first recognized in full by E. NOETHER [14] and in current field theories — where the internal degrees of freedom have not be taken into account — were discussed by several authors in details [15].

As a new and perhaps important result of our above considerations not the formal generalization of NOETHER's theorem has to be held according to which the internal motion of the physical systems induces new constants of motion too, however, the following recognition seems to be more remarkable: Owing to the connection between the local co-ordinate system of the momentum-space and the original frame of reference $\mathfrak{K}$ in the co-ordinate-space, mentioned above in connection with the passive interpretation of co-ordinate transformations, in fact, continuous LORENTZ transformations of the co-ordinate-space correspond also to the discontinuous internal transformations (such as reflexions and inversions in respect to the λ-trieder). Indeed, the internal inversion (in other words the change of the handedness of the λ-trieder), *e. g.*, may be reached by continuous rotations in the four-dimensional co-ordinate-space. This means, however, that if the internal space can be interpreted in physical terms, then new constants of motion can be derived corresponding to the intrinsic properties of physical fields.

§ 8. *Discussions*

Collect the most important geometrical properties of the internal space pointed out above:

(a) The internal space is three-dimensional;

(b) The group $\mathcal{G}_{\xi}$ of the transformations of the internal space — *i. e.*, the group of transformations of the λ-trieder considered — is isomorphic with the three-dimensional rotary-reflexion group;

(c) The constants of motion corresponding to the symmetry transformations of the group $\mathcal{G}_{\xi}$ determine internal attributes of elementary particles and that of the associated physical fields, respectively;

(d) The constants of motion referring to the internal attributes of elementary particles as well as the mass-spectrum of free fields prove the reality of the internal space and that of the internal degrees of freedom.

The results *(a)*—*(c)* suggest the connection, and — what is more — the identification of the internal space with the threedimensional isospace. Indeed, our more recent investigation [2] proved that the isotransformations can be interpreted in geometrical terms and several laws of conservation (such as *PC*, *PZ*, *PP'* theorems *etc.*) were justified.* The interpretation of isotransformations and the intrinsic

* In our paper [2] Eq. (12) means too radical condition for the field component ψ which may be fulfilled only by very special functions. This condition can, however, be omitted, namely, it was not used in the following.

constants of motion based on NOETHER's theorem will be investigated in the next future.

Now, consider a special property of physical fields induced in a line-element space $\{x^\mu, p^\mu\}$ or $\{x^\mu, \xi_i\}$. As it has been emphasized above several times, the field components are depending on the line-elements. Due to the physical interpretation of the homogeneous direction co-ordinates in the case of hyper quantization the operators $\mathbf{p}^\mu$ associated with the momentum p^μ, and the operators $\mathbf{x}^\mu$ associated with the co-ordinates x^μ, as well as the operators $\psi_\alpha(x^\mu, \mathbf{p}^\mu)$ do not commute by pairs. This means, however, that beside the usual commutators of the current field theories also the commutator $[\mathbf{x}^\mu, \psi_\alpha]$ has to be defined. This can analogously be done by BORN's reciprocity transformation [17]:

$$x^\mu \to p^\mu, \quad p^\mu \to -x^\mu \tag{8,1}$$

as it is well-known in the case of YUKAWA's bilocal theory of fields [6—8]. In fact, this analogy refers to an intrinsic connection between the suggested theory and that of YUKAWA previously emphazised.

Finally, the problem arises how the anisotropy of the phasespace has to be interpreted philosophically? In order to carry out a possible interpretation, let us discuss shortly the philosophical cencept of the space-time continuum.

Independent of their concrete material content, all events of the material world take place *in space* (side by side) and *in time* (one after another) as well. This means, however, that the events of the material world can be characterized by four objective parameters: by three data mapping their side-by-sideness (place) and by one determining their succession (time-point). As a matter of fact, the whole of material events can be regarded as a four-dimensional ensemble of events denoting it in terms of A. D. ALEXANDROV [18] as *the space of events*, or rather in the more usual terms of the theory of relativity — also considering that, in fact, all of the material events are continuously dependent on each other — as the *space-time continuum.* From this point of view *the space of events must be the absolute existential form of the material world.*

Nevertheless, the real physical events can only be truly mapped in this way if the geometrical connections among the „points" of the space of events — which are realized in the geometrical structure of the space-time continuum — by objective connections among the corresponding events, *i. e.*, by real material interactions, are determined. This means, however, that the spacetime continuum, or rather its geometrical structure depends on the concrete material content, *i. e.*, on special physical interactions, of the material world. As matters stand, the space-time continuum and its geometrical structure, respectively, which correspond to the whole of material events and their objective interactions as well, are unified in the dialectical unity of form and content. From this point of view *the space of events is relative;* indeed, its structure is determined by the concrete features of matter.

Due to these considerations — to be summarized — the space of events and the space-time continuum, respectively, is the objective existential form of the material world and *by the philosophical cathegory of space-time continuum the absolute and relative features of space and time are represented.* This can also be expressed by saying that the space-time continuum — in spite of the previous metaphysical concept of space and time according to which the EUCLIDIAN character of

space and the absoluteness of time would be an *a priori* cathegory of human mind — cannot be a bare passive and from the matter independent geometrical background of physical processes; but, its structure is determined by objective interactions. J. BOLYAI was the first scientist who already hundred years ago suggested this idea; then it was recalled by RIEMANN and finally, as a principal idea of EINSTEIN's theory of gravitation has been scored its revolutional success in macro-physics. So far, this point of view is generally accepted in up-to-date physics.

Nevertheless, the gravitational interactions can be neglected in micro-physics. Therefore, in the case of elementary particles — owing to EINSTEIN'theory — it is usually supposed that the structure of the space-time would be pseudo-EUCLIDIAN. Hence, if we take seriously into account the suggested point of view, one can say that the pseudo-EUCLIDIAN character of the space-time world, *i. e.* its homogenity and isotropy, is rather a consequence of the special symmetry properties of the actual interactions than an *a priori* feature of space-time. In fact, if *e. g.*, the violation of parity conservation can be regarded as a special property of weak interactions, it seems that from the anisotropy of these interactions also the anisotropy of the space may be concluded. The reason that the structure of the space-time world is in most of the cases isotropic, seems to be that the anisotropy of the weak interactions are overlapped by the electromagnetic and strong interactions which have higher or at least another symmetry character. This can also be expressed by saying that the strict insistence of the *a priori* EUCLIDIAN (or pseudo-EUCLIDIAN) structure of the space-time world can be regarded as a rest of the metaphysical concepts.

Our recent investigations in this direction have been based on the supposition that in the anisotropic internal structure of the elementary particles the anisotropy of the space-time continuum would appear. This supposition may be illustrated in simple terms as follows:

In anisotropic spaces the structure of the space is characterized not only by its curvature, but by its torsion too. If the general idea could be accepted that the anisotropy of the space-time world is determined by the anisotropy of the interactions, it should be supposed, of course, that the longitudinal polarization of the particles may be induced by the torsion of the anisotropic space-time. Consider the following analogy: In the case of the gravitational field the photon with zero rest mass is the most adequate test particle which moves on a geodetical line of the space-time world. As a matter of fact, the deflexion of light in the neighbourhood of the Sun, *e. g.*, proves curvature of the space-time continuum. Analogously, the neutrino seems to be a similar test particle to the photon among the fermions to observe the torsion of the space-time. Indeed, its rest mass is zero — so that during its motion adapts perfectly itself to the structure of the space-time — and its longitudinal polarization is a maximal one, so far that the two-component theory of neutrino is aware of one kind of neutrinos with helicity (-1). In these terms one can say that the longitudinal polarization of elementary particles demonstrates the space-time anisotropy.

This was the reason that we have recently suggested the unfamiliar idea that the strict adherence to the *a-priority* of the pseudo-EUCLIDIAN space-time structure would be responsible for the problems connected with the violation of parity conservation predicted by LEE and YANG [19]. In other words, it may be supposed that the structure of our physical world as a consequence of anisotropic interactions seems to be richer than it was previously supposed [20].

In terms of the new development of the suggested theory one can say that in the anisotropy of the phase-space the anisotropy of the space-time is reflected, determined by special physical interactions. For the sake of simplicity it was, however, supposed that the dynamism of the local change of the space-time structure due to the anisotropic interactions has provisionally not to be investigated; but, in fact, only the consequences of the actual anisotropy of the space-time world — in the case of different but specialized fields — were discussed. Furthermore, it was supposed that the anisotropy of the space-time can be characterized by the longitudinal polarization of the field quanta which can be regarded as a constant anisotropy parameter $\mathscr{P}$. Nevertheless, this means only a provisional supposition. Indeed, in a field theory — considering also the interactions of fields — this constant anisotropy parameter has to be changed by an anisotropy parameter which depends on space and time: $\mathscr{P}=\mathscr{P}(x^{\mu})$ determined by the interactions of fields to be considered. This problem has, however, to be discussed in the future in detail.

* * *

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ВНУТРЕННЯЯ СТРУКТУРА ФИЗИЧЕСКИХ ПОЛЕЙ

Я. И. Хорват

Свилеватость элементарных частиц, значит правая и левая анизотопия были объяснены с помощью формализма относительного фазового пространства. Таким образом предложено новое обоснование теории, описанной в предыдущей работе, кроме того выведены уравнения пространства из принципа вариации, дан масс-спектр барионов, обобщена теорема *Нётера*. Преобразования, определяемые в пространстве изоспина, можно заменить непрерывными преобразованиями в координатном пространстве. Наконец были описаны философские понятия континуума пространства-времени и интерпретация предложенного метода.

INVESTIGATIONS IN THE FIELD OF DIOLS AND CYLIC ETHERS. IV

Preparation of 2-monosubstituted derivatives of trimethylene oxide

by M. BARTÓK and A. S. GILDE

Institute of Organic Chemistry, József Attila University, Szeged

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The authors have reviewed the literature of syntheses of 2-monosubstituted four-membered cyclic ethers. The syntheses of 2-methyl, 2-ethyl, 2-n-propyl, 2-phenyl and recently 2-n-butyl, 2-t-butyl, 2-c-hexyl and 2-benzyloxetanes have been realized. It has been stated that these cyclic ethers can be prepared with a relatively good yield (mean 70%) from chloroacetates containing the corresponding primary chlorine.

The previous communication [1] dealt with the synthesis, the physical and physico-chemical properties and structure of trimethylene oxide. The present subject of the paper is the synthesis of 2-alkyl, 2-cycloalkyl and 2-aryl derivatives of trimethylene oxide.

There are two ways for synthesizing 2-monosubstituted oxetanes as regard to the preparation of starting substances and the method of ring closure:

1. The method starting from 1,3-diols, and
2. Synthesis starting from 1,3-chlorohydrins and chloroacetates, respectively.

1. After a thoroughful examination of literature we can state that so far experiments to synthesize four-membered cyclic ethers were undertaken in three directions:

a) Several investigators have dealt with the intramolecular dehydratation of 1,3-diols, however, most of the experiments failed to lead to trimethylene oxide and to its substituted derivatives [e. g. 2, 3, 4, 5]. The dehydration was effected under different conditions. Attempts to dehydrate 1,3-diols in the gaseous phase, in the presence of different catalysts, are in progress in the Institute of Organic Chemistry of the University of Szeged, too. To prepare oxetanes a new method was described by SCHMOYER and CASE [6, 7], who started from 1,3-diols. This process cannot be regarded as a pure intramolecular dehydration.

b) Oxetanes could be prepared by the catalytic pyrolysis of cyclic carbonates of the corresponding substituted 1,3-diols. This method was applied with success only in the synthesis of 3,3-disubstituted trimethylene oxides [8]. Of the 2-substituted oxetanes the method gained application only for the synthesis of methyl derivatives and according to the infrared spectrum of the crude product it gave a very low yield (15%).

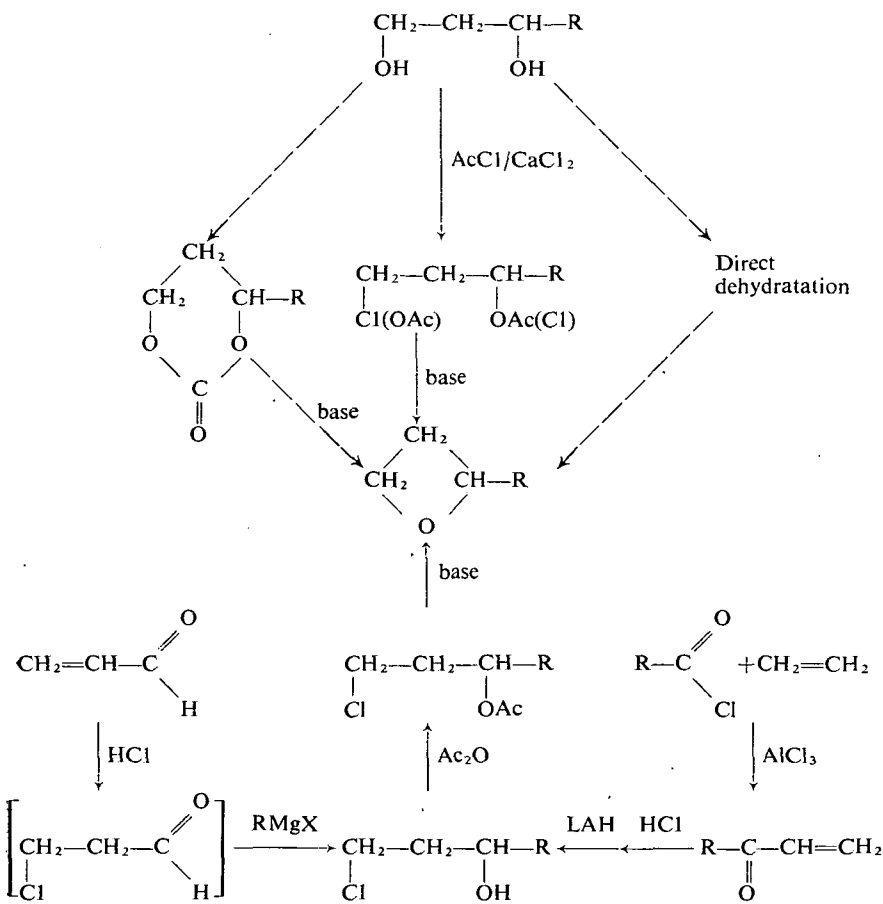
c) The corresponding four-membered cyclic ether could be prepared from 1,3-diols through chloroacetate too. This method is connected with the second one.

The method was applied only for 2-methyloxetane [9, 10]. We shall extend this to the synthesis of 2-monosubstituted oxetanes, a report of which will be published later. The general way of synthesis is as follows: preparation of the corresponding 1,3-diol in the simplest way (*e. g.* by the GRIGNARD reaction of *β*-oxypropionaldehyde, or by the REFORMATSKII reaction or by the PRINS reaction) from which chloroacetate is prepared in one step and the alkaline ring closure of the latter results in the formation corresponding oxetanes.

2. On the basis of experiments so far carried out, 2-substituted oxetanes were prepared with the best yield by alkaline ring closure starting from 1-R-3-chloropropanol-1, where R = alkyl and aryl, resp. The literature reports the syntheses of the following 2-substituted four-membered cyclic ethers: 2-methyloxetane [11, 12, 13, 14, 15], 2-ethyloxetane [16, 14, 15], 2-n-propyloxetane [14], 2-phenyloxetane [15].

Possibilities rendered by the synthesis are shown in Table I.

Table I.
Preparation of 2-R-oxetanes



In the following we examine somewhat more extensively data of the literature regarding the preparation of 2-monosubstituted oxetanes. The first method will be the subject of another publication, thus this time we do not go into details only wish to turn attention to the possibilities to synthesize alkyl and aryl, respectively, 1-substituted derivatives of 1,3-propanediol. β-oxypropionaldehyde [17, 18, 19, 20] and some aldehydes, easy to obtain, could serve as starting materials of the synthesis. The required 1,3-diol can be obtained from the former by the GRIGNARD reaction and from the latter from β-oxycarbonic acid, prepared either by a reaction with ketene or by the REFORMATSKII synthesis [21]. 1,3-butanediol is a commercial preparate (CHEMISCHE WERKE HÜLS, BDH, LIGHT's). Previously it has been mentioned that to synthesize 2-monosubstituted oxetanes, literature mostly mentions the application of chlorohydrins and chloroacetates, respectively, containing primary chlorine atom. When in the chlorohydrin molecule the chlorine atom is connected to a secondary carbon atom, under the conditions of alkaline ring closure the transformations does not result in formation of oxetane (a detailed study of these reactions is in progress). Chlorohydrins containing primary chlorine atom are easy to prepare from acrolein. From the latter compound β-chloropropionaldehydeis formed under anhydrous conditions, below -10 °C, on effect of hydrochloric acid, and from it the required chlorohydrin can be prepared with alkyl magnesium halides. The acrolein and hydrochloric addition was studied first by ADAM, CARTMELL, GEUTHER and GRIMAUX [22, 23]. The reaction has been dealt with more recently, too; it received manyfold application in the syntheses [24, 25, 26, 27, 28, 29, 30, 31, 16, 32, 14, 13]. The addition of hydrochloric acid, owing to the electron attractive effect of the carbonyl group, is contrasted to the MARKOWNIKOFF empiric rule [33]. Starting from acrolein, chlorohydrins can be prepared in about 30% yield. (The reason of this relative low yield is the rapid polymerisation of β-chloropropionaldehyde on temperature higher than -10 °C it easily trimerizes). Therefore the GRIGNARD reaction must be carried out immediately after the addition of hydrochloric acid without the isolation of β-chloropropionaldehyde. Literature contains the following syntheses of chlorohydrins: 1-methyl [30, 14, 13]; 1-ethyl-[29, 30, 16, 14]; 1-n-propyl-[29, 30, 14]; 1-i-propyl-[14] and 1-i-amyl-3-chloropropanol-1 [29].

Chlorohydrins containing primary chlorine atom are easy to prepare from α, β-unsaturated ketones, obtained by the reaction of the corresponding acid chlorides with ethylene on effect of $AlCl_3$ or $SnCl_4$. On effect of hydrogen chloride the latter can be converted in to β-chloroethly-alkyl and aryl ketones, respectively, and from them chlorohydrins are formed by reduction with $LiAlH_4$. The first step of the process can be directed so that immediately β-chloroethyl-alkyl and aryl, ketones are formed. The reaction between acid chlorides and olefines, on effect of metal chlorides above mentioned, was first described by BLANC and KRAPIVIN [34, 35]. If the corresponding acid chlorides are available, instead of starting from acrolein, this method can be applied with success because of the very good yield. There is a special method to prepare β-chloroethyl-phenyl-ketone, when it is synthesizing it from β-chloropropionyl chloride and benzene by the FRIEDEL—CRAFTS reaction [36, 37, 38, 39]. There are descriptions in the literature for the syntheses of the following β-chloroethyl-alkyl and aryl ketones, starting from acid chlorides: methyl- [40, 41, 42, 12]; ethyl- [40, 41, 32, 15]; n-propyl- [40, 41]; n-butyl- [40, 41]; and phenyl β-chloroethyl ketones [43, 44, 45]. The reaction of olefines and acid chlorides

on effect of $AlCl_3$ is dealt with by THOMAS in his book published in 1941 [46]. Other methods are also available for the syntheses of β-chloroketones. E. G. β-chloroketones were prepared by the reaction of β-chloropropionyl chloride with organic zinc compounds [47] and by the chloromethylation of ketones in the presence of zinc chloride [48].

For the reduction of β-chloroketones by which we can get to the corresponding 1,3-chlorohydrins. SONDHEIMER, SEARLES and their coworkers gave descriptions [12, 15].

3-monosubstituted oxetanes are prepared by alkaline ring closure of the acetylated products of chlorohydrins mentioned above. In this respect we can find exceptions in the literature. Namely FORSBERG [14] synthesized oxetanes direct by the alkaline reaction of chlorohydrins. Using this was as Table II indicates the yield of cyclic ethers is lower than starting from chloroacetates. The mechanism of these conversions will be described in a following paper.

Now we wish to give a short review of the literature on the preparation of 2-monosubstituted oxetanes.

The first description of a synthesis of 2-methyloxetane is given in a patent [11]. 1-chlorobutanol-3 was prepared from 1,3-butanediol — (we are of the opinion that as a result of the reaction of 1,3-butanediol with hydrochloric acid, 3-chlorobutanol also forms) — which was closed to a ring in the presence of sodium hydroxide. FORSBERG [14] has prepared 2-methyloxetane from 1-chlorobutanol-3, obtained from acrolein. GAYLORD and his coworkers [13] followed a similar, method however, carried out the ring closure of chloroacetates obtained by the acetylation of chlorohydrins. 2-methyl-trimethylene oxide was prepared also from mixtures of chloroacetate obtained by the reaction of 1,3-butanediol with acetylchloride [9, 10]. The same compound was prepared from β-chloroethyl-methyl ketone received by the reaction of acetyl chloride and ethylene in the presence of aluminum chloride [12, 15]. The formation of cyclic ether was observed also in the catalytic decomposition of 4-methyl-1,3-dioxan-2-on but this method, owing to the low yield, cannot be regarded as the proper way of synthesizing 2-methyloxetane. SCHMOYER and CASE [7] in their new method prepared 2-methyl-trimethylene oxide direct from 1,3-butanediol, so that concentrated sulphuric acid solution of diol was added dropwise to boiling alkali.

In literature we can find three descriptions of the preparation of 2-ethyltrimethylene oxide. LESPIEAU [16] started from acrolein through chlorohydrin and chloroacetate, FORSBERG [14] followed a similar method but he started from chlorodydrin, SEARLES and his coworkers [15] prepared 2-ethyloxetane from chloroketone obtained from the reaction of β-chloropropionyl chloride with ethylene in the presence of aluminum chloride, via chloroacetate.

2-n-propyl and i-propyloxetanes were prepared by FORSBERG [14] by alkaline ring closure of chlorohydrins, obtained from acrolein.

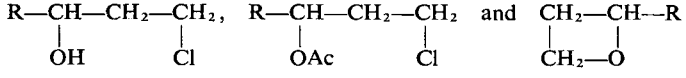
The synthesis of 2-phenyltrimethylene oxide was undertaken by SEARLES and his coworkers [15]. β-chloroketone, the starking material was prepared by the FRIEDEL—CRAFTS reaction [39]. They converted chloroketone to chlorohydrin and to chloroacetate, and by the alkaline ring closure of the latter 2-phenyloxetane was obtained. This step was also carried out direct by with chlorohydrin, but the yield was lower.

Data in literature on the % yield of 2-monosubstituted oxetanes and the starting materials of the different syntheses are summarized in Table II.

In the course of our researches of the cyclic ethers, we are dealing with the syntheses, study of the mechanism of the formations, and chemical transformations of trimethylene oxide derivatives. So far we have prepared 2-methyl-, ethyl-, n-propyl-, i-propyl-, n-butyl-, t-butyl-, c-hexyl-, phenyl-, and benzyl-oxetanes. 2-methyl-trimethylene oxide was prepared by an alkaline ring closure (as described by SEARLES and coworkers [10]) with a yield of 50% of chloroacetates obtained by MELTZER and KING's method [49] from 1,3-butanediol. At the same time we repeated SONDHEIMER's [12], further GAYLORD and his coworkers' [13] methods. Here the yield

Table II.

Yield in per cent of



No	R	Yield %		Yield %		Yield %		Ref.
		a	b	a	b	a	b	
1	methyl	—[f]				20		11
2	methyl	79[d]	76	95	92	66	62	12
3	methyl	33	31	83	80	68	60	13
4	methyl	~16				35		14
5	methyl			70[c]		42		9
6	methyl	—[f]		—[f]		55		15
7	methyl			83[c]	84	52	50	10
8	methyl					~21		7
9	methyl					15		8
10	ethyl	—[f]	31	—[f]	86	—[f]	62	16
11	ethyl	~27				51		14
12	ethyl	71		96		60		15
13	*n*-propyl	~21	34		83	46	62	14
14	*i*-propyl	~23	33		85	48	63	14
15	*n*-butyl		30		85		85	
16	*t*-butyl		28		87		74	
17	*c*-hexyl		40		85		75	
18	phenyl	87[e]	85	83	81	70	70	15
19	phenyl	87[e]				58		15
20	phenyl		30		80		68	
21	benzyl		26		80		68	

a data in literature
b data in Experimental of this paper
c mixture of two isomers of chloroacetate
d yield of chloroketone was 61%
e yield of chloroketone was 93%
f yield % was not given by the authors
g vacant places — the authors did not deal with the synthesis of the compound

was 62 and 60%, respectively. The syntheses of all other 2-substituted oxetane derivatives were carried out starting from acrolein, according to the method already mentioned, by alkaline ring closure of the corresponding chloroacetates. 2-phenyl-trimethylene oxide was also prepared starting from phenylvinyl ketone. Table II gives the yields of the subsequent steps of the syntheses as compared with data ovailable in the literature. These data show that the yield of cyclic ether, as a rule, is above 60%. From the yields obtained with compounds having increasing substitutents at the 2-position unequivocal deductions cannot be made. We think that a more exact evaluation will be possible from results of kinetic investigations. The main reaction is accompained by other by — reactions and the conversion, is followed by secondary processes too. These processes will be discussed in our paper dealing with the mechanism of alkaline reactions of 1,3-chlorohydrins and 1,3-chloroacetates.

Experimental

Table III summarizes physical constants of chlorohydrins, chloroacetates and oxetanes, mentioned in the paper.

Tables IV, V and VI show the physical contants and results of mikroanalysis of the compounds described in *Experimental.*

Synthesis of 3-chloro-1-butylacetate and 4-chloro-2-butyl-acetate isomers were carried out according to MELTZER and KING [49]. The reaction mixture was cooled with ice and NaCl. Acetyl chloride was added during a period of about 3 hours and the temperature was rised to 20°C. The mixture of the two isomers was prepared from 1000 g 1,3-butanediol in 84% yield.
Boiling point 75—7°C (18 mm).
Analysis: Calculated for $C_6H_{11}O_2Cl$

	C: 47,85	H: 7,36	Cl: 23,54
Found:	C: 47,76	H: 7,28	Cl: 23,60.

4-chloro-butanon-2. The synthesis was carried out by [12]. Ethylene was prepared by dehydration of ethylalcohol on γ-aluminum oxide at 400°C. From the reactor, after cooling with ice, a mixture of vapour and gas was bubbled through sodium hydroxide solution, concentrated sulphuric acid and heated calcium chloride, and then it was introduced to the reaction mixture. After corresponding purification the crude product was fractionated. Yield: 386 g (56%). B. p. 60°C (28 mm); n_D^{26}: 1,4298 (reported (12) b. p. 47°C (16 mm); n_D^{27}: 1,4299).

β-chloropropionaldehyde. A calculated amount of hydrogen chloride (100 g) bubbled through concentrated sulphuric acid and dry calcium chloride was introduced into 200 ml abs. etheric solution of 168 g acrolein (3 mole) with vigorous stirring, below —10°C. The cooling is realised with a dry ice-aceton mixture, or if it is not possible, with ice and NaCl. Working with this latter, during the introduction of hydrogen chloride depending on the insulation of the bottle containing the cooling mixture and the on amount of the latter, the ice salt mixture must be changed two-four times. With effective cooling the introduction of hydrogen chloride requires two-three hours. After the absorption of the gas in the required quantly, the etheric solution is mixed continously with 20—20 g of dry sodium carbonate and calcium

Table III.

Data on the physical constants of

$$R{-}\underset{\underset{OH}{|}}{CH}{-}CH_2{-}\underset{\underset{Cl}{|}}{CH_2}, \quad R{-}\underset{\underset{OAc}{|}}{CH}{-}CH_2{-}\underset{\underset{Cl}{|}}{CH_2} \quad \text{and} \quad \underset{\underset{CH_2{-}O}{|}}{CH_2}{-}\underset{|}{CH}{-}R$$

No	R	Name	Boiling point C°	(Hg mm)	d gr/cm³	n_D (t°)	Ref.
1.	methyl	4-chloro-butanol-2	67	(20)	—	1,4408 (26)	12
2.	methyl	4-chloro-butanol-2	63,7—64	(15)	$1{,}0686^{20}_{4}$	1,4430 (20)	14
3.	methyl	4-chloro-butanol-2	61	(10)	—	1,4440 (20)	10
4.	methyl	4-chloro-2-butyl-acetate	70	(16)	—	1,4260 (25)	12
5.	methyl	4-chloro-2-butyl-acetate	71—2	(16)	—	1,4273 (20)	10
6.	methyl	2-methyloxetane	59,4—7	(736)	$0{,}8480^{20}_{20}$	1,3889 (20)	11
7.	methyl	2-methyloxetane	60	(747)	—	1,3890 (25)	51
8.	methyl	2-methyloxetane	60—61	(762)	—	1,3894 (25)	12
9.	methyl	2-methyloxetane	59—60	—	—	1,3886 (25)	13
10.	methyl	2-methyloxetane	60—60,5	(756)	$0{,}8494^{20}_{4}$	1,3910 (20)	14
11.	methyl	2-methyloxetane	59,7—8	—	—	1,3919 (20)	9
12.	methyl	2-methyloxetane	59	—	—	1,3913 (20)	15
13.	methyl	2-methyloxetane	60	—	—	1,3913 (20)	10
14.	methyl	2-methyloxetane	58—61	—	—	—	7
15.	ethyl	1-chloro-pentanol-3	77—77,5	(20)	$1{,}0327^{25}$	1,448 (20)	16
16.	ethyl	1-chloro-pentanol-3	77,3—77,9	(17,5)	$1{,}0427^{20}_{4}$	1,4482 (20)	14
17.	ethyl	1-chloro-pentanol-3	82	(25)	—	1,4435 (20)	15
18.	ethyl	1-chloro-3-acetoxy-pentane	81	(13)	$1{,}03896^{24}$	1,431 (24)	16
19.	ethyl	1-chloro-3-acetoxy-pentane	82—4	(20)	—	1,4310 (20)	15
20.	ethyl	2-ethyloxetane	88,5—89	(748)	$0{,}8481^{20}$	1,4072 (20)	16
21.	ethyl	2-ethyloxetane	78,9	(759)	$0{,}8483^{20}_{4}$	1,4000 (20)	14
22.	ethyl	2-ethyloxetane	87	(730)	0,850	1,4040 (20)	15
23.	*n*-propyl	1-chlorohexanole-3	78,8—79,2	(9)	$1{,}0132^{20}_{4}$	1,4488 (20)	14
24.	*n*-propyl	2-n-propyloxetane	108—9	—	$0{,}8494^{20}_{4}$	1,4112 (20)	14
25.	*i*-propyl	1-chloro-4-methyl-pentanol-3	72,8—74,0	(10,5)	$1{,}0233^{20}_{4}$	1,4510 (20)	14
26.	*i*-propyl	2-*i*-propyloxetane	91,5—92	(753)	$0{,}8480^{20}_{4}$	1,4080 (20)	14
27.	phenyl	1-chloro-3-phenyl-propanol-3	130—2	(8)	—	—	52
28.	phenyl	1-chloro-3-phenyl-propanol-3	75	(0,03)	—	1,5412 (20)	15
29.	phenyl	1-chloro-3-phenyl-3-acetoxypropane	84—5 52	(0,1) (0,5)	—	1,5121 (20)	15
30.	phenyl	2-phenyloxetane	87—8	(8)	$1{,}023^{20}_{4}$	1,5288 (20)	15

Table IV.

Physical properties of

No	R	Formula	Molecular weight	Boiling point C° (Hg mm)	d_4^{20} gr/cm³
1.	methyl	C_4H_9ClO	108,57	67– 8 (20)	1,069
2.	ethyl	$C_5H_{11}ClO$	122,60	75– 6 (15)	1,044
3.	*n*-propyl	$C_6H_{13}ClO$	136,62	81– 2 (10)	1,012
4.	*i*-propyl	$C_6H_{13}ClO$	136,62	72– 3 (10)	1,020
5.	*n*-butyl	$C_7H_{15}ClO$	150,64	100– 2 (3)	0,997
6.	*t*-butyl	$C_7H_{15}ClO$	150,64	90– 2 (3)	1,005
7.	*c*-hexyl	$C_9H_{17}ClO$	176,68	138–40 (10)	1,075
8.	phenyl	$C_9H_{11}ClO$	170,50	125– 6 (6)	1,155
9.	benzyl	$C_{10}H_{13}ClO$	184,52	140– 2 (2)	1,137

Table V.

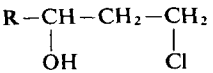
Physical properties of

No	R	Formula	Molecular weight	Boiling point C° (Hg mm)	d_4^{20} gr/cm³
1.	methyl	$C_6H_{11}ClO_2$	150,60	98–100 (35)	1,058
2.	ethyl	$C_7H_{13}ClO_2$	164,64	75– 6 (9)	1,037
3.	*n*-propyl	$C_8H_{15}ClO_2$	178,66	89– 90 (9)	1,019
4.	*i*-propyl	$C_8H_{15}ClO_2$	178,66	83– 4 (3)	1,026
5.	*n*-butyl	$C_9H_{17}ClO_2$	192,68	82– 4 (1)	1,002
6.	*t*-butyl	$C_9H_{17}ClO_2$	192,68	76– 80 (1)	1,014
7.	*c*-hexyl	$C_{11}H_{19}ClO_2$	218,72	125– 6 (2,5)	1,071
8.	phenyl	$C_{11}H_{13}ClO_2$	212,54	136– 7 (2)	1,143
9.	benzyl	$C_{12}H_{15}ClO_2$	226,56	124– 8 (2)	1,141

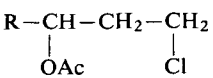
Table VI.

Physical properties of

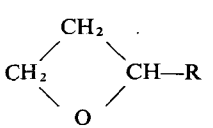
No	R	Formula	Molecular weight	Boiling point C° (Hg mm)	d_4^{20} gr/cm³
1.	methyl	C_4H_8O	72,10	59–60 (750)	0,847
2.	ethyl	$C_5H_{10}O$	86,13	87– 8 (748)	0,844
3.	*n*-propyl	$C_6H_{12}O$	100,16	110– 1 (753)	0,842
4.	*i*-propyl	$C_6H_{12}O$	100,16	102– 3 (753)	0,832
5.	*n*-butyl	$C_7H_{14}O$	114,18	141– 2 (753)	0,845
6.	*t*-butyl	$C_7H_{14}O$	114,18	132– 3 (742)	0,837
7.	*c*-hexyl	$C_9H_{16}O$	140,22	67– 9 (10)	0,936
8.	phenyl	$C_9H_{10}O$	134,17	76– 7 (4)	1,041
9.	benzyl	$C_{10}H_{12}O$	148,19	72– 4 (10)	1,063



n_D^{20}	R_{M_D}		C %		H %		Cl %	
	found	calc.	found	calc.	found	calc.	found	calc.
1,4438	26,98	27,06	44,49	44,20	8,31	8,35	32,67	32,66
1,4478	31,43	31,68	48,75	49,0	8,91	9,05	28,78	28,92
1,4487	36,20	36,30	52,68	52,74	9,66	9,58	26,00	25,96
1,4520	36,12	36,30	52,65	52,74	9,63	9,58	26,06	25,96
1,4533	40,86	40,92	55,82	55,81	9,85	10,04	23,20	23,54
1,4563	40,77	40,92	55,72	55,81	9,90	10,04	23,24	23,54
1,4890	47,43	47,95	61,50	61,20	9,84	9,68	19,82	20,00
1,5402	46,35	46,50	63,17	63,35	6,46	6,49	20,74	20,78
1,5406	50,98	51,15	65,10	65,12	6,84	7,08	18,84	19,25



n_D^{20}	R_{M_D}		C %		H %		Cl %	
	found	calc.	found	calc.	found	calc.	found	calc.
1,4278	36,58	36,53	48,03	47,85	7,53	7,36	23,54	23,54
1,4318	41,16	41,18	50,94	51,20	7,90	7,95	21,13	21,60
1,4352	45,78	45,83	53,82	53,79	8,39	8,46	19,70	19,85
1,4403	45,94	45,83	53,87	53,79	8,38	8,46	19,66	19,85
1,4390	50,56	50,48	55,95	56,20	8,80	8,89	18,25	18,41
1,4452	50,61	50,48	56,14	56,20	8,71	8,89	18,33	18,41
1,4720	57,19	57,56	60,70	60,41	8,95	8,75	16,10	16,18
1,5124	55,81	56,02	62,04	62,12	6,24	6,16	16,86	16,68
1,5218	60,53	60,67	63,43	63,60	6,60	6,67	15,21	15,65



n_D^{20}	R_{M_D}		C %		H %	
	found	calc.	found	calc.	found	calc.
1,3909	20,21	20,11	—	66,60	—	11,20
1,4028	24,90	24,73	68,46	69,77	11,34	11,63
1,4110	29,54	29,35	70,87	71,96	12,00	12,06
1,4066	29,61	29,35	71,35	71,96	11,94	12,06
1,4195	34,15	33,97	72,95	73,63	12,24	12,38
1,4157	34,21	33,97	73,18	73,63	12,30	12,38
1,4644	41,31	41,01	76,66	77,08	11,59	11,50
1,5296	40,04	39,87	80,21	80,51	7,40	7,46
1,5540	44,68	44,52	80,74	81,02	8,08	8,16

chloride for about 10—10 minutes. After precipitation the solution is carefully filtered through cotton into a bottle formerly cooled below —10 °C (-or into a dropping funnel belonging to a beforehand constructed apparatus, containing the GRIGNARD reagent). The solution thus obtained was used direct for the Grignard reaction without isolation.

4-*chloro-butanol*-2 was prepared after the reduction of chloro-ketone by lithium aluminum hydride [12]. 300 g (76%) of chlorocarbinol was obtained from 386 g 4-chloro-2-butanol. The synthesis of the compound from β-chloropropionaldehyde with magnesium iodide was also carried out in the following manner. Etheric solution of β-chloropropionaldehyde, prepared from 3 mole acrolein, was added dropwise from a double -walled dropping funnel (-in order to avoid trimerisation of β-chloropropionaldehyde, the temperature was maintained below —10 °C by means of ice-NaCl cooling between the two walls) to the absolute etheric solution of the GRIGNARD reagent prepared from 3 mole of magnesium (73 g) 3 mole of methyl idoide (426 g) and 1400 ml abs. ether, so that during the addition (2—3 hours) the temperature did not rise above 0 °C, and then the mixture was stirred for an hour at room temperature. Following this the addition product was decomposed with aqueous acetic acid solution of somewhat larger amount than calculated (200 g acetic acid/100 ml water), under cooling. The aqueous phase was extracted with ether, and the combined etheric extractions were washed with sodium carbonate solution, dried over heated sodium carbonate and distilled. 100 g (31%) 4-chloro-2-butanol was obtained from 168 g (3 mole) acrolein.

4-*chloro*-2-*butylacetate*. The acetylation of chlorocarbinol can be performed with acetyl chloride in the presence of pyridine, or in a simpler way but with worse yield, with acetic anhydride. Both methods were applied for the preparation of 4-chloro-2-butylacetate. The acetylation with acetyl chloride has been published (12). Acetylation with acetic anhydride was carried out as follows: a few drops of concentrated sulphuric acid and then 1.45 mole of acetic anhydride were added to 1,2 mole of chlorocarbinol during 30 minutes, under constant stirring. The reaction is exothermic. Then the mixture was refluxed during 1,5 hours in an oil bath and the excess anhydride carefully decomposed with some water. The organic layer was separated from the aqueous one, washed with water and aqueous sodium carbonate solution. The combined and neutralized phases were extracted with ether. The organic phases were also combined, dried over anhydrous sodium carbonate and fractionated. 140 g of 4-chloro-2-butylacetate was obtained from 180 g of 4-chloro-2-butanol. Yield: 80%.

2-*methyloxetane*. A 2 litre three-necked bottle was equipped with a strong stirrer, thermometer, dropping funnel and a 40 cm VIGREUX column. The column was connected with a well-cooled descending cooler. 500 g of chloroacetate mixture was added dropwise to the mixture of 600 g of potassiumhydroxide, 600 g of sodiumhydroxide and 60 ml water, with vigorous stirring, at 140 °C during a period of about two-three hours. In such an addition the rate of distillation is about 1 drop/sec. The bottle was heated in an oil bath so that oil reached the neck of the bottle. After introduction the temperature of the oil bath was raised to 160 °C and kept there for an hour. The crude product was dried with potassiumhydroxide and fractionally distilled from metallic natrium. Yield.: 120 g (50%).

Chlorohydrines enlisted in Table IV, chloroacetates in Table V and oxetanes in Table VI were prepared starting from 3-3 mole acrolein, according to the method

described at 2-methyloxetane. The corresponding Grignard reagents were prepared from ethyl bromide, n-propyl bromide, i-propyl bromide, n-butyl bromide, t-butyl chloride, c-hexil chloride, bromobenzene and benzyl chloride, according to the descriptions in Organic Syntheses. Acetylation was in every case carried out with acetic anhydride.

β-chloropropiophenon was prepared starting from 2 mole benzoylchloride by MATSUMOTO's method [45].

1-*phenyl*-3-*chloro-propanol*-1 was prepared by the reduction of the former with lithium aluminum hydride by the method used for the reduction of β-chloroethyl-ketone.

Mole refractions were calculated applying VOGEL's data [50].

* * *

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ИЗУЧЕНИЕ ХИМИЧЕСКИХ ПРЕВРАЩЕНИЙ ДИОЛОВ И ОРГАНИЧЕСКИХ ОКИСЕЙ. IV

ПРИГОТОВЛЕНИЕ 2-ОДНОЗАМЕЩЕННЫХ ПРОИЗВОДНЫХ ОКИСИ ТРИМЕТИЛЕНА

М. Барток и А. Ш. Гильде

Авторы дают обзор о методах синтеза 2-однозамещенных четырехчленных органических окисей. Они приготовили 2-метил-, 2-этил-, 2-и-пропил-, 2-фенил- и в последнее время 2-н-бутил-, 2-т-бутил-, 2-ц-гексил- и 2-бензил-β-окиси. Авторы высказывают, что эти циклические эфиры могут быть приготовлены сравнительно хорошим выходом (общее 70%) из хлороацетатов содержащих соответствующий первичный хлор.

INVESTIGATIONS IN THE FIELD OF DIOLS AND CYCLIC ETHERS. V

Preparation of 2-monosubstituted derivatives of tetrahydropyran

By N. I. SHUIKIN, I. F. BELSKII and R. A. KARAKHANOV

Institute of Organic Chemistry N. D. Zelinskii of the Academy of Sciences, USSR, Moscow

B. KOZMA and M. BARTÓK

Institute of Organic Chemistry, József Attila University, Szeged

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In the course of studying the contact catalytic transformations of cyclic ethers in the gas-phase, investigation of tetrahydropyran derivatives was also undertaken. The present communication reports a modified synthesis of 2-monosubstituted six-membred cyclic ethers, required for the experiments.

In the course of the study of the contact catalytic and vapour-phase transformations of cyclic ethers, their isomerisation to oxo-compounds has also been studied [1, 2, 3]. In the present paper we report our work on the synthesis of 2-monosubstituted derivatives of tetrahydropyran, required for the above experiments. During our syntheses we have also dealt with the preparation of 2-monosubstituted derivatives of tetramethylene oxide. Oxetane derivatives are synthesized by the alkaline ring closure of 1,3-chloroacetates in a yield of about 70%. The preparation of cyclic ethers by the intramolecular dehydration of 1,3-diols has not been successful up to now.

The study of literature shows that the first attempts to synthesize tetrahydropyran derivatives applied directly the intramolecular water cleavage reaction of diols. The dehydration of diols in the presence of sulphuric acid first was examined in a more detailed manner by FRANKE and his coworkers [4, 5, 6, 7]. They have described the syntheses of some 2-monosubstituted tetrahydropyran derivatives.

A remarkable progress in the development of the synthesis of 2-monosubstituted tetrahydropyran derivatives was brought by a completely new method of synthesizing dihydropyran, elaborated and published in 1933 by PAUL [8]. He prepared 2,3-dihydropyran from a very cheap and easily obtainable starting substance, i. e. from furfurol, by hydrogenation under pressure. This way he first got tetrahydrofurfuryl alcohol and from it 2,3-dihydropyran in one step. The novelty in this method was the obtainment of the compound in a continuous system on aluminum oxide catalyst, at 380 °C. After elaborating the large-scale synthesis of 2,3-dihydropyran, PAUL had studied its chemical transformations and 2-bromotetrahydropyran was prepared by addition of hydrogen bromide [9, 10] to the 2,3-dihydro compound, and the reaction of the

2-bromo derivative with the GRIGNARD reagent resulted in corresponding 2-alkyl- and aryl-derivatives, respectively [11, 12].

After this short introduction we give a report on the literature of the synthesis of 2-monosubstituted tetrahydropyran. FRANKE [6] had also prepared 2-methyltetrahydropyran by the intramolecular dehydration of diol, however, the exact description of the synthesis was given only by PAUL in 1938 [13]. He started from 2-(α-furyl)-methyl carbinol, which is prepared in two steps from furfurol. He got 2-methyl-5,6-dihydropyran by dehydration, and its hydrogenation resulted in 2-methyltetrahydropyran. PAUL prepared the compound also from 2-bromotetrahydropyran [14], and by the method above mentioned [3]. The required compound was synthesized by COLONGE and LASFARGUES [15] by the isomerisation of hexen-5-ol-1 with phosphoric acid, in a yield of 72%. COLONGE and GIRANTET according to their paper, published this year, prepared 2-methyltetrahydropyran in the following way: 2-furancarbonic-acid-methylesther was converted to 5-methyl-2-carbometoxi furan by a FRIEDEL—CRAFTS reaction. By a two step reduction of RANEY Ni and with lithium aluminum hydride, 2-oxymethyl-5-methyl furan was obtained and from this 2-methyl tetrahydropyran prepared in the known way by intramolecular dehydration and hydrogenation on RANEY Ni. Other derivatives were also synthesized in the same way, they will be referred to at the corresponding place. They prepared 2-ethyl tetrahydropyran from 2-bromotetrahydropyran with ethylmagnesiumbromide [11, 14, 13] with a yield of 76% [12].

2-n-propyltetrahydropyran was also prepared from 2-bromotetrahydropyran and n-propylmagnesiumbromide [11, 14, 13] with 86% yield [12]. FRANKE [6] synthesized it, too, from diol by dehydration.

2-i-propyltetrahydropyran was prepared by COLONGE and GIRANTET by the way already described [16].

2-n-butyltetrahydropyran was prepared by PAUL [14], BELSKII and SHUIKIN [3] from 2-bromotetrahydropyran by the GRIGNARD reaction; FRANKE and LIEBERMAN [5, 6] prepared it from diol by dehydration with sulphuric acid, while SMITH, NORTON and BALLARD applied the hydrogenation of dihydropyran derivatives formed by the dien type condensation of acrolein and hexene-1. 2-t-butyltetrahydropyran was synthesized by COLONGE and GIRANTET [16].

2-n-amyltetrahydropyran was prepared by the dehydration of diol with sulphuric acid in a yield of 62% [6, 18].

2-t-amyltetrahydropyran was synthesized also by the above authors in the already known method [16].

Tetrahydropyran substituted at the position 2 with a phenyl radical was first prepared by PAUL, by means of the GRIGNARD reaction of 2-bromotetrahydropyran with phenylmagnesiumbromide [11, 12, 14]. SMITH and his coworkers got to the compound in question by the condensation of acrolein with styrene followed by hydrogenation [17]. Data in literature on the syntheses and main physical constants of 2-monosubstituted tetrahydropyran derivatives are summarized in Table I.

In the course of study of the contact catalytic transformations of cyclic ethers in the gas-phase, experiments were carried out with six-membered cyclic ethers, too.

The present paper reports the synthesis of 2-monosubstituted tetrahydropyran, required for our experiments. From the study of data available in the literature it can be stated that the preparation in laboratory of the compounds in question can

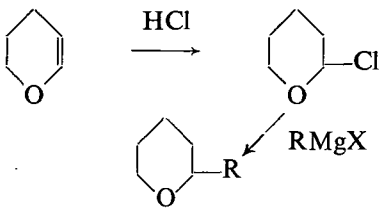
Table I

Data in literature on the preparation and physical constants of 2-monosubstituted tetrahydropyrans

No	Name	Yield in %	Boiling point °C	(mm)	d gr/cm³	n_D (t°C)	References
1.	2-methyl-THP	—	104—6	(770)	$0{,}866^{13}_{15}$	1,42355 (13)	13 1938
2.	2-methyl-THP	—	101—103	(758)	$0{,}868^{11}$	1,42175	14 1938
3.	2-methyl-THP	—	101—102	(750)	$0{,}8570^{20}_{4}$	1,4187 (20)	3 1959
4.	2-methyl-THP	72	103	(750)	$0{,}852^{20}_{4}$	1,418 (20)	15 1962
5.	2-methyl-THP	—	101—2	(750)	$0{,}851^{25}_{4}$	1,4160 (25)	16 1962
6.	2-ethyl-THP	—	128—9	(770)	$0{,}865^{15}_{20}$	1,42885 (15)	11 1934
7.	2-ethyl-THP	76	128—9	(770)	$0{,}865^{15}_{15}$	1,42885 (15)	12 1935
8.	2-ethyl-THP	—	128—9	(773)	$0{,}869^{10}$	1,42985	14 1938
9.	2-ethyl-THP	—	128—9	(752)	$0{,}8566^{20}_{4}$	1,4245 (20)	3 1959
10.	2-*n*-propyl-THP	—	152—3	(760)	$0{,}860^{15}_{15}$	1,43256 (15)	11 1934
11.	2-*n*-propyl-THP	86	152—3	(760)	$0{,}860^{15}_{15}$	1,43256 (15)	12 1935
12.	2-*n*-propyl-THP	—	153—4	(768)	$0{,}866^{9}$	1,43407	14 1938
13.	2-*n*-propyl-THP	—	152—3	(745)	$0{,}8552^{20}_{4}$	1,4290 (20)	3 1959
14.	2-*i*-propyl-THP	—	142,5	(750)	$0{,}857^{25}_{4}$	1,4308 (25)	16 1962
15.	2-*n*-butyl-THP	—	175—7		—	—	5 1922
16.	2-*n*-butyl-THP	—	64	(14)	$0{,}865^{10}$	1,43818	14 1938
17.	2-*n*-butyl-THP	—	63—5	(14)	—	1,4368 (20)	17 1951
18.	2-*n*-butyl-THP	—	176—7	(750)	$0{,}8570^{20}_{4}$	1,4350 (20)	3 1959
19.	2-*t*-butyl-THP	—	157	(750)	$0{,}857^{25}_{4}$	1,4350 (25)	16 1962
20.	2-*n*-amyl-THP	62	84	(14)	—	—	6 1929
21.	2-*n*-amyl-THP	—	73,7—74	(10)	—	—	18 1935
22.	2-*n*-amyl-THP	—	198,5—200,5	(747)	—	—	18 1935
23.	2-*t*-amyl-THP	—	103	(71)	$0{,}880^{25}_{4}$	1,4515 (25)	16 1962
24.	2-phenyl-THP	—	113	(11)	$1{,}020^{15}_{20}$	1,53191 (15)	11 1934
25.	2-phenyl-THP	74	113	(11)	$1{,}02^{18}_{15}$	1,5319 (18)	12 1935
26.	2-phenyl-THP	—	111—2	(10)	$1{,}0229^{11}$	1,53183	14 1938
27.	2-phenyl-THP	—	105—6	(10)	$1{,}0145^{20}$	1,5273. (20)	17 1951

be carried out in the simplest, quickest and most profitable method starting from dihydropyran, which can be obtained in very large quantity. The corresponding cyclic ether can be obtained more easily by the dehydration of 1,5-diols, but the preparation of the starting material is rather lengthy. In the synthesis we have applied PAUL's basic conception. As it is known, PAUL had prepared 2-bromotetrahydropyran from dihydropyran by adding HBr, and the C—Br bond, which is easy to polarize, enters a reaction with the GRIGNARD reagent, and this results in the corresponding 2-substituted tetrahydropyran derivative.

Our synthesis differs so that we have started from 2-chlorotetrahydropyran, the preparation of which is already described in literature [19—22]. The addition of hydrogen chloride to dihydropyran can be performed much more easily than the addition of hydrogen bromide. Hydrogen chloride gas is easier to obtain than hydrogen bromide, and the purification of the latter from bromide is rather complicated. The preparation of the compounds was carried out according to the following scheme:



R = methyl, ethyl, n-propyl, i-propyl, n-butyl, t-butyl, c-hexyl, phenyl and benzyl.

In the course of choosing (and improving) this process the following considerations were taken besides the forementioned facts: the 2-positioned chlorine atom of cyclic ethers (of ethers in general) can be easily polarized due to the well known reasons, thus it easily reacts. The chemical properties of the chlorine atom at the position 2 in the tetrahydrofuran series were far-reachingly discussed [23, 24]. It a report has been published recently on its reaction with the GRIGNARD reagent [25].

2-chlorotetrahydropyran is an instable compound, it decomposes even if allowed to stand. Its purification by distillation brings therefore great losses. It is purposeful to carry out the synthesis so that afterr the calculated amount of hydrogen chloride had dessolved the formed 2-chlorotetrahydropyran should be added dropwise (without any purification) direct to the dry etheric solution of the formerly prepared GRIGNARD reagent.

Experimental

Dihydropyran was *BDH* product. B. p. 85 – 86 °C; d_4^{20}: 0,918; n_D^{20}: 1,4400.

2-*chlorotetrahydropyran.* 1000 ml three-necked bottle was equipped with a stirrer, a gas-inlet tube and a thermometer. The third hole was closed with a tube containing anhydrous calcium chloride. 252 g dihydropyran (3 mole) was measured into the bottle and the content cooled with a mixture of ice and NaCl. Calculated amount of hydrogen chloride (105 g), dried with concentrated sulphuric acid and calcium chloride was introduced with stirring, at a rate that the temperature had not risen above 0 °C. The time required for the introduction of hydrogen chloride was about 2—3 hours.

In order to determine the physical constants of the obtained product, it was redistilled. B. p.: 54—55 °C (26 mm); n_D^{24}: 1,4660.

2-alkyl, c-alkyl, aryltetrahydropyran. The corresponding GRIGNARD reagents were prepared from 3 mole of metalic magnesium and 3 mole of R—X according to the methods described in Organic Syntheses. The following halogenides were applied in the preparation of the GRIGNARD reagent: methyliodide, ethylbromide, n-propylbromide, i-propylbromide, n-butylbromide, t-butylchloride, c-hexylchloride, bromobenzol and benzylchloride.

To the dry etheric solution of the corresponding GRIGNARD reagent, cooled with ice-NaCl mixture, dry etheric solution of crude 2-chlorotetrahydropyran, prepared from dihydropyran, was added dropwise, under intensive stirring in a ratio of 1:1. To avoid decomposition of 2-chlorotetrahydropyran a double walled dropping funnel, cooled with icy water, was used. The time of addition is about two hours. After introduction the mixture it was allowed to stand at room temperature and stirred for two hours, then 1000 ml 5% acetic acid was added dropwise to it, under further stirring. The layers thus formed were separated. The aqueous layer was extracted twice with ether. The combined organic phases were washed with saturated aqueous sodium hydrocarbonate and dried over dry K_2CO_3. After removing of the ether, it was fractionated. The yield, calculated for dihydropyran was generally 65—85%.

Physical contants of the formed 2-monosubstituted tetrahydropyran derivatives are given in Table II.

Table II.

Physical properties of 2-monosubstituted tetrahydropyrans

No	R	Formula	Molecular weight	Boiling point C°	(Hgmm)
1.	methyl	$C_6H_{12}O$	100,16	102—3	(752)
2.	ethyl	$C_7H_{14}O$	114,18	127—8	(751)
3.	*n*-propyl	$C_8H_{16}O$	128,21	152—3	(746)
4.	*i*-propyl	$C_8H_{16}O$	128,21	144—5	(752)
5.	*n*-butyl	$C_9H_{18}O$	142,23	176—7	(750)
6.	*t*-butyl	$C_9H_{18}O$	142,23	157—8	(752)
7.	*c*-hexyl	$C_{11}H_{20}O$	168,27	122—4	(30)
8.	phenyl	$C_{11}H_{14}O$	162,22	106—8	(10)
9.	benzyl	$C_{12}H_{16}O$	176,25	130—5	(10)

d_4^{20} g/cm³	n_D^{20}	R_{M_D} found	R_{M_D} calctd.	C% found	C% calctd.	H% found	H% calctd.
0,856	1,4186	29,52	29,66	—	71,95	—	12,08
0,856	1,4245	34,07	34,08	73,28	73,62	12,22	12,35
0,855	1,4294	38,69	38,86	74,71	74,97	12,31	12,58
0,860	1,4315	38,63	38,86	74,82	74,97	12,25	12,58
0,857	1,4352	43,32	43,51	75,68	75,98	12,60	12,75
0,860	1,4361	43,25	43,51	75,92	75,98	12,62	12,75
0,932	1,4729	50,62	50,60	78,32	78,51	11,76	11,98
1,020	1,5300	49,13	49,06	81,29	81,43	8,53	8,69
1,030	1,5408	53,76	53,71	82,12	81,76	8,81	9,15

* * *

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ИЗУЧЕНИЕ ХИМИЧЕСКИХ ПРЕВРАЩЕНИЙ ДИОЛОВ И ОРГАНИЧЕСКИХ ОКИСЕЙ. V

ПРИГОТОВЛЕНИЕ 2-ОДНОЗАМЕЩЕННЫХ ПРОИЗВОДНЫХ ТЕТРАГИДРОПИРАНА

Н. И. Шуйкин, И. Ф. Бельский, Р. А. Караханов, Б. Козма и *М. Барток*

При изучении контактно-каталитических превращений циклических соединений в газовой фазе, авторы изучали также производных тетрагидропирана. Настоящая работа дает отчет о модифицированном синтезе 2-однозамещенных шестичленных органических окисей нужных для экспериментов.

ÜBER DIE MANNICH-KONDENSATION VON NITRO-HYDROXY-ACETOPHENONEN

Von GY. SIPOS und I. DOBÓ

Institut für Angewandte Chemie der József Attila Universität, Szeged

und B. MATKOVICS

Institut für Organische Chemie der József Attila Universität, Szeged

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Nitro-hydroxy-acetophenone wurden in Gegenwart von Salzsäure als Katalysator mit Formaldehyd und Piperidinhydrochlorid kondensiert. Der Einfluss der Versuchsbedingungen und Substituenten auf die Reaktion wurde untersucht. Es konnte festgestellt werden, daß sich die Reaktion mit den besten Ausbeuten in einem Benzol-Nitrobenzol Lösungsmittelgemisch abspielt. Die Untersuchung der Reaktion der Hydroxy- und Nitroacetophenone unter den gleichen Bedingungen zeigte, daß die entsprechenden Aminoketone bei den angewandten Reaktionsparametern aus dem ortho-Hydroxy-acetophenon und den in ortho-Stellung mit einer Hydroxylgruppe substituierten Nitro-hydroxy-acetophenonen nicht bilden, im Falle der Nitro-acetophenone und der keine ortho-Hydroxygruppe enthaltenden Nitro-hydroxy-acetophenone jedoch entstehen.

Wir führten die MANNICH-Kondensation einiger Nitro-hydroxy-acetophenone mit Formaldehyd und Piperidinhydrochlorid in Gegenwart von Salzsäure als Katalysator durch. Als Lösungsmittel wurde Alkohol, Benzol, Benzol-Nitrobenzol sowie Nitrobenzol verwendet. Mit Ausnahme des Alkohols spielte sich die Reaktion in diesen Lösungsmitteln ab. Die besten Ausbeuten konnten im Benzol-Nitrobenzol Lösungsmittelgemisch erhalten werden [1], was darauf schlissen läßt, dass die Entfernung des gebildeten Wassers den größten Einfluss auf die Ausbeteu ausübt (Tab. I).

Im Zusammenhange mit der Reaktionsdauer konnte festgestellt werden, daß die Ausbeute über einer optimalen Reaktionsdauer sowohl bei der Anwendung von Benzol-Nitrobenzol als auch in Nitrobenzol alleine abzunehmen beginnt. Die optimale Reaktionszeit ist in Nitrobenzol in der Regel kürzer als in Benzol-Nitrobenzol oder Benzol (Tab. I), woraus geschlossen werden kann, dass das Dipolmoment des angewandten Lösungsmittels die Reaktionsgeschwindigkeit möglicherweise beeniflusst.

Aus der Reihe der Nitro-hydroxy-ketone reagiert das 4- und 5-Nitro-2-hydroxy-acetophenon unter den obigen Bedingungen nicht. Kein entsprechendes Aminoketon bildete sich unter diesen Bedingungen auch aus dem ortho-Hydroxy-acetophenon. Bei dieser Reaktion konnte ein definierbares Produkt weder wesentlich drastischeren noch unter milderen Reaktionsparametern isoliert werden. Aus dem gesagten geht also hervor, dass die Hydroxylgruppe in den eine ortho-Hydroxylgruppe enthaltenden

Acetophenonen den Ablauf der Kondensation verhindert. Es gelang auch nicht, die Reaktion in Gegenwart von Natronlauge als Katalysator durchzuführen, da aus den Analyseergebnissen der erhaltenen Produkte darauf geschlossen werden kann, dass diese Ketone als Phenole reagieren. Keine Reaktion spielte sich auch beim

Tabelle I.

-phenyl-3-piperidino--propanon-1-hydrochlorid	Benzol-Nitrobenzol Zeit (Stdn.)	Ausbeute %	Nitrobenzol Zeit (Stdn.)	Ausbeute %	Benzol Zeit (Stdn.)	Ausbeute %
1-(-3-Nitro-4-hydroxy-)-	1 1/2	10,73	1/2	22,5	—	—
	3	30,68	3	—	3	21,5
	6	40,54	6	—	6	28,6
	9	50,5	—	—	—	—
	12	19,7	—	—	—	—
1-(-6-Nitro-3-hydroxy-)-	6	72,3	1 1/2	14,1	—	—
	8	44,66	3	64,9	3	38,6
	9	keine	6	22,1	6	31,4
1-(-4-Nitro-3-hydroxy-)-	5	12,34	1/2	7,15	—	—
	9	34,8	3	6,8	3	45,6
	12	29,2	—	—	6	37,9
1-(-2-Nitro-3-hydroxy-)-	3	6,1	1/2	—	—	—
	6	33,85	3	25,02	3	43,9
	9	4,09	6	23,06	6	25,06
1-(-2-Nitro-3-hydroxy-)-	6	33,8	6	35,9	—	—

Tabelle II.

-phenyl-3-piperidino--propanon-1-hydrochlorid	Benzol-Nitrobenzol Zeit (Stdn.)	Ausbeute %	Nitrobenzol Zeit (Stdn.)	Ausbeute %	Benzol Zeit (Stdn.)	Ausbeute %
1-(-4-Nitro-)-	3	31,9	1/2	22,3	—	—
	6	42,8	1 1/2	30,2	—	—
	9	43,2	3	33,9	6	29,4
1-(-3-Nitro-)-	3	36,6	1 1/2	18,2	—	—
	6	40,25	3	22,9	—	—
	9	42,2	9	8,52	6	24
1-(-2-Nitro-)-	3	34,3	1 1/2	24,6	—	—
	6	35,2	3	30,1	—	—
	9	13,8	6	39,3	—	—
1-(-4-Hydroxy-)-	1 1/2	15,9	—	—	—	—
	6	35,5	4	20,2	4	24,5
	9	7,2	—	—	—	—

Versuch der Kondensation des meta-Hydroxy-acetophenons ab, bzw. es entstand ein nicht difinierbares Polymerprodukt. Die Polymerisation spielte sich in diesem Falle schon bei Raumtemperatur, ca. 1/4 Stunde nach dem Vermischen der Reaktionspartner ab. Die Kondensation des para-Hydroxy-acetophenons spielte sich demgegenüber unter den angewandten Reaktionsbedingungen mit guter Ausbeute ab (Tab. II).

Außer den Hydroxy-acetophenonen wurde die Kondensation unter den oben erwähnten Bedingungen auch mit den Nitro-acetophenonen durchgeführt.

Im Falle der Nitro-acetophenone, unter Anwendung von Benzol-Nitrobenzol Lösungsmittelgemisch nahm die Ausbeute mit der Verlängerung der Reaktionsdauer kaum zu. Nur beim ortho-Nitro-acetophenon konnte festgestellt werden, daß die Ausbeute bei einer Reaktionszeit von 9 Stunden um ca. auf 1/3 abgenommen hat.

Die durch uns hergestellten Verbindungen sind in Tabelle 3 zusammengefasst.

Mit dem 1-(-3-Nitro-4-hydroxy-)-phenyl-3-piperidino-propanon-1-chlorhydrat wurden pharmakologische Untersuchungen durchgeführt. Dabei wurde festgestellt, daß die Verbindung über eine nikotinartige Wirkung verfügt, einen ganglienerregenden Effekt ausübt und einen Anstieg von Blutdruck und Atemfrequenz — z. B. bei Katzen — verursacht. Die Wirkung ist intensiver, wenn die Verbindung nicht intravenös sondern intraarteriell verabreicht wird. Zur Herbeiführung der erwähnten Wirkung wären bei Katzen 5 mg/kg Körpergewicht notwendig, während, die tödliche Dosis 200 mg/kg betrug. Die erwähnten Effekte werden durch TEA gehemmt.

* * *

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*Experimenteller Teil**

Durchführung der Kondensationen

a) In Alkohol (2)

0,18 g (1 mMol) Keton und 0,12 g (1 mMol) Piperidinhydrochlorid wurden in 5 ml abs. Alkohol suspendiert, dann wurden 0,05 g 73%-iges Paraformaldehyd und 2 Tropfen konzentrierte Salzsäure zugegeben und das Gemisch wurde 1,5 Stunden hindurch gekocht. Es folgte Zugabe von weiteren 1,05 g Paraformaldehyd und weiteres dreistündiges Sieden. Das Reaktionsgemisch wurde über Nacht in den Kühlschrank gestellt. Je nach der Qualität des Ketons schied sich in einigen Fällen eine feste Substanz aus. War dies nicht der Fall, so wurde das Reaktionsgemisch an freier Luft eingedampft. In den meisten Fällen gelang es, sowohl das als Ausgangsmaterial verwendete Keton wie auch das Piperidinhydrochlorid vollständig oder teilweise zurückzuerhalten.

b) In Benzol-Nitrobenzol (1)

0,1 g (0,55 mMol) Keton, 0,10 g (0,80 mMol) Piperidinhydrochlorid und 0,05 g 73%-iges Paraformaldehyd wurden in 1 ml eines Benzol-Nitrobenzol Gemisches (1:1) suspendiert und nach Ansäuern mit 2 Tropfen konzentrierter

* Die Schmelzpunkte sind unkorrigiert.

Salzsäure auf dem siedenden Wasserbade in einem solchen System erwärmt (Reaktionszeiten siehe Tabelle), das mit einer mit Benzol beschickten Wasserfalle versehen war. Die Auflösung des Stoffes kann infolge der Ausscheidung des Reaktionsproduktes nicht beobachtet werden. Nach der angebenen Reaktionszeit wurde das Gemisch für 24 Stunden im Kühlschrank beiseitegestellt, dann filtriert, der Niederschlag mit kaltem Athylacetat gewaschen und an der Luft getrocknet. Die erhaltene Substanz wurde unter gleichzeitiger Behandlung mit Entfärbungskohle aus heissem absolutem Athanol umkristallisiert. Ausbeuten siehe Tabelle.

c) In Nitrobenzol

Verwendet wurden die gleichen Stoffmengen wie unter b), als Lösungsmittel diente das gleiche Volumen Nitrobenzol. Die übrigen Reaktionsbedingungen und die Aufarbeitung des Reaktionsgemisches sind die gleichen, die auch unter b) geschrieben wurden.

d) In Benzol

Die Reaktionen wurden mit den gleichen Stoffmengen und unter den gleichen Bedingungen durchgeführt wie unter b), die Menge des Lösungsmittels betrug jedoch 2 ml. Die übrigen Reaktionsbedingungen und die Aufarbeitung des Reaktionsgemisches waren die gleichen, die unter b) bereits beschrieben wurden.

Die mit den Kondensationen zusammenhängenden wichtigsten Daten sind in Tabelle III zusammengefaßt.

Tabelle III.

-phenyl-3-piperidino--propanon-1-HCl	Kristallformen	Schmp.	Bruttoformel	Mol. Gew.	Berechnet N	Cl	Gefunden N	Cl
1-(-3-Nitro-4--hydroxy-)-	Weisse Nadeln	196°	$C_{14}H_{19}O_4N_2Cl$	314,7	8,9	11,2	8,6	10,4
1-(-6-Nitro-3--hydroxy-)-	Gelbliche Nadeln	136°	,,	,,	,,	,,	8,7	10,4
1-(-2-Nitro-5--hydroxy-)-	Weisse Nadeln	139°	,,	,,	,,	,,	8,4	—
1-(-2-Nitro-3--hydroxy-)-	Knochenfarbene Kristallnadeln	202°	,,	,,	,,	,,	8,7	10,0
1-(-4-Nitro-3--hydroxy-)-	Lebhaft gelbe Kristallnadeln	187°	,,	,,	,,	,,	8,7	10,8
1-(-4-Nitro-)-	Gleblichweisse Kristalle	202°	$C_{14}H_{19}O_3N_2Cl$	298,7	9,3	11,8	8,9	11,8
1-(-3-Nitro-)-	Weisse Kristalline Substanz	171°	,,	,,	,,	,,	9,4	11,0
1-(-2-Nitro-)-	Gelbliche Kristallnadeln	192°	,,	,,	,,	,,	—	11,11
1-(-4-Hydroxy-)-	Weisse Kristalline Substanz	199°	$C_{14}H_{20}O_2NCl$	269,7	5,1	13,1	5,0	13,2

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О КОНДЕНСАЦИИ НИТРО-ГИДРОКСИ- АЦЕТОФЕНОНОВ МАННИХА

Г. Шипош, И. Добо, Б. Маткович

Конденсировались нитдо-гидрокси-ацетофеноны формальдегидом и пиперидин-гидроклоридом в присутствии катализатора хлористоводородной кислоты. Было рассмотрено действие на реакцию обстоятельств, а также замещенных.

ÜBER DIE DARZENS-KONDENSATION VON NITRO-HYDROXY-PHENACYLBROMIDEN. II

Von GY. SIPOS, B. CZUKOR und I. DOBÓ

Institut für Angewandte Chemie der József Attila Universität, Szeged

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Es wurde die Darzens-Kondensation mit verschiedenen Nitro-hydroxy-phenacylbromiden — auch mit HCl als Katalysator — erfolgreich durchgeführt und einige neure Beobachtungen bezüglich der Herstellung von Phenacylbromiden gemacht.

Als Forsetzung einer früheren Arbeit [1] haben wir die in Tabelle 1 angeführten Phenacylbromide hergestellt.

Tabelle I.

Die dargestellten Nitro-hydroxy-phenacylbromide

Nr.	-phenacaylbromid	Ausb. %	Schmp.	Summenformel	Molgew.	Halogen Ber.	Halogen Gef.	Kohlenstoff Ber.	Kohlenstoff Gef.	Wasserstoff Ber.	Wasserstoff Gef.
1.	2-Nitro-3-hydroxy-	35	97°	$C_8H_6O_4NBr$	260,0	30,7	30,6	36,9	—	2,3	—
2.	4-Nitro-3-hydroxy-	30	89°	$C_8H_6O_4Br$	260,0	30,7	—	36,9	37,1	2,3	2,6
3.	6-Nitro-3-hydroxy	20	90°	$C_8H_6O_4NBr$	260,0	30,7	30,1	36,9	—	2,3	—

Die Entfärbung der Lösung war bei der Darstellung dieser Verbindungen, entsprechend unseren bisherigen Erfahrungen, zunächst gefolgt und erst dann die Bromwasserstoffentwicklung eintritt.

Die Bromierung der drei, meta-hydroxy-Gruppe enthältenden Nitro-hydroxy--acetophenone (Tab. I.) hat mit schwacherer Ausbeute stattfindet als die Bromierung der zwei, orto-hydroxy-Gruppe enthältenden Nitro-hydroxy-acetophenone (Tab. II).

Diese Erfahrung ist erklärlich mit der Wirkung der orto- und para-Stellung der Nitro-Gruppe und der meta-Stellung der Hydroxyl-Gruppe.

Die Ketone können verhältnismäßig unter milden Bedingungen bromiert werden (Tab. II), da die Wechselwirkung zwischen der Oxo- und der Hydroxy-Gruppe [1] weniger zur Geltung kommt, als im Falle der Wasserstoffbrücke enthältenden Nitro-hydroxy-acetophenone (4-Nitro-2-hydroxy- und 5-Nitro-2-hydroxy-acetophenon).

Wir haben die Bromierung der Ketone zwecks Ausschaltung der wahrscheinlich konkurrenten Ringbromierungsreaktion auch mit N-Brom-sukcinimid versucht, was aber erfolglos blieb.

Tabelle II.

Die Bedingungen der Darstellung von Nitro-hydroxy-phenacylbromide

Nr.	-acetophenon	Im Eisessig				In Chloroform			
		Entfärbungstemp. C°	Erwärmungszeit	Erwärmungstemp. C°	Ausbeute von Phenacyl bromid	Entfärbungstemp. C°	Erwärmungszeit	Erwärmungstemp. C°	Ausbeute von Phenacylbromid %
1.	3-Nitro-4-hydroxy	55	—	55	45	39	15 Min	39	60
2.	4-Nitro-3-hydroxy	61	10 Min	61	30	50	10 Min	40	30
3.	2-Nitro-3-hydroxy	63	5 Min	offene Flamme	35	54	10 Min	54	30
4.	6-Nitro-3-hydroxy	61	Verschiedene	Verschiedene	—	63	10 Min	63	1—2
5.	5-Nitro-2-hydroxy	83	5 Min	offene Flamme	50	—	—	—	—
6.	4-Nitro-2-hydroxy	89	10 Min	offene Flamme	50	—	—	—	—

Die Reaktion der dargestellten unbekannten Nitro-hydroxy-phenacylbromide mit Benzaldehyd und 4-Nitro-benzaldehyd lieferte die entsprechenden Epoxy-ketone (Tab. III.), aber mit Anisaldehyd reagierten sie nicht. Diese Ergebnisse stützt die früheren Feststellungen bezüglich der reaktionsbeeinflußende Wirkung der Aldehydsubstituenten unter [2—5].

Tabelle III.

Die dargestellten Epoxy-Ketone (bei Anwesenheit von Base als Katalisatot)

Nr.	-aethylen-oxyd	Ausbeute %	Schmp. C°	Aussehen	Summenformel	Mol.-gew.	Analyse	
							Ber.	Gef.
1.	1-(Phenyl)-2-(2-nitro--3-hydroxy-benzoyl)	55	115	orangengelbe Plättchen	$C_{15}H_{11}O_5N$	285,2	C 63,1 H 3,8	63,0 3,7
2,	1-(4-Nitro-phenyl-)-2--(2-nitro-3-hydroxy--benzoyl)-	65	173	gelbe Säulen	$C_{15}H_{10}O_7N_2$	330,2	N 8,4	8,6
3.	1-(4-Nitro-phenyl)-2-(4-nitro-3-hydroxy-benzoyl)-	40	196	zitronen-gelbe Nadeln	$C_{15}H_{10}O_7N_2$	330,2	N 8,4	8,1
4.	1-(4-Nitro-phenyl-)-2-(6-nitro-3-hydroxy--benzoyl)-	40	196	hellgelbe Nadeln	$C_{15}H_{10}O_7N_2$	330,2	N 8,4	8,0

In Verbindung mit der Epoxybildung, haben wir bei Raumtemperatur, mit gleichen und relativ geringen Katalysatorkonzentrationen, den Einfluß der Reaktionsdauer auf die Ausbeute und die Qualität des Produkts studiert. Es zeigte sich dass auch innerhalb gleicher Katalysatorkonzentrationen die frühere Festellung [5] gültig ist, wonach die längere Reaktionsdauer die günstigere ist und die der Ausbeute zutage tretenden Unterschiede relativ gering sind (Tab. IV. und V.).

Da nach den bisheringen Literaturangaben [6, 7] und auch auf Grund unserer eigenen Untersuchungen, aus den Nitro-phenacylbromiden unter den obigen Bedingungen die entsprechenden Ketone nicht entstehen, wird im Falle der Nitro-

Tabelle IV.

Die Darzens-Kondensation von 3-Nitro-4-hydroxy-phenacylbromid und 4-Nitro-benzaldehyd

Katalysator	Katalysator konz. %	Reaktionszeit	Roher Schmp. C°	Rohe Ausb. %	Nach Umkrist.	
					Schmp. C°	Ausb. %
NaOMe	0,5	0,5 Std	178—196	70	201	54
NaOMe	0,5	4,0 Std	169—191	75	202	59
NaOMe	0,5	16,0 Std	170—190	80	204	62

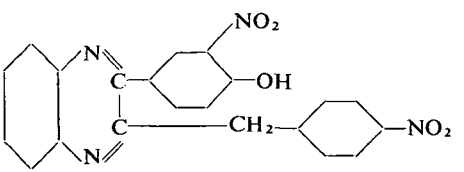
Tabelle V.

Die Darzens-Kondensation von 2-Nitro-3-hydroxy-phenacylbromid und 4-nitro-benzaldehyd

Katalysator	Katalysator konz. %	Reaktionszeit	Roher Schmp. C°	Rohe Ausb. %	Nach Umkrist.	
					Schmp. C°	Ausb. %
NaOH	0,25	5 Min	156—166	43	169	35
NaOH	0,25	10 Min	144—160	47	167	38
NaOH	0,25	16 Std	164—169	61	171	57

hydroxy-phenacyl-bromide das Eintreten der Kondensationen wahrscheinlich durch die Gegenwart der Hydroxylgruppe ermöglicht. Zwecks der Klärung dieses Problems wurde auch die Darzens-Kondensation der 2- und 4-Hydroxy-phenacylbromid untersucht, aber diese Verbindung lieferte die entsprechende Epoxy-Ketone mit Benzaldehyd und 4-Nitro benzaldehyd unter den angewandten Bedingungen nicht. Es reagierten mit den Aldehyden auch die isomeren Nitro-phenacylbromide nicht.

Zwecks der weiteren Klärung der Struktur des 1-(4-Nitro-phenyl)-2-(3-nitro-4-hydroxy-benzoyl)-aethylenoxyds [5] wurde das durch ihr Kochen mit konz. HCl erhaltenen 3-Nitro-4-hydroxy-phenyl-4-nitro-benzyl-glyoxal (4) mit Ortophenylendiamin zur Reaktion gebracht und dadurch das 2-(3-Nitro-4-hydroxy-phenyl)-3-(4-nitro-benzoyl)-kinoxalin gewonnen:



Es gelang die Darzens-Kondensation auch bei Anwesenheit von Salzsäure als Katalysator zu verwirklichen (Tab. VI).

Unter den mildesten Bedingungen und mit der besten Ausbeute gelang die Durchführung der Säure-Kondensation mit dem 3-Nitro-4-hydroxy-phenacylbromid [1]. Sie gelang auch mit 4-Nitro-3-hydroxy und 2-Nitro-3-hydroxy-phenacyl-bromid, allerdings unter wesentlich energischeren Bedingungen. Die Säure-Kondensation war mit 2-Hydroxy-, 4-Nitro-2-hydroxy- und 5-Nitro--2-hydroxy-phenacyl-bromid, d. h. mit den auch eine Ortho-hydroxygruppe enthaltenden Phenacylbromiden nicht durchzuführen. Das 4-Hydroxy-phenacylbromid

Tabelle VI .

Die dargestellten Epoxy-Ketone (bei Anwesenheit von HCl *als Katalysator)*

Nr.	-aethylenoxyd	Katalysator %	Katalysator konz. %	Reaktionszeit	Reaktions-temperatur	Schmp. C°	Misch-Schmp. C°
1.	1-(4-Nitro-phenyl)--2-(3-nitro-4-hydroxy-benzoyl)-	HCl	35	90 Std.	Raumtemperatur	202	202
2.	1-(4-Nitro-phenyl)--2-(4-nitro-3-hydroxy-benzoyl)-	HCl	35	40 Min.	Rückfluss-tempe-ratur	196	195
3.	1-(4-Nitro-phenyl)--2-(2-nitro-3-hydroxy-benzoyl)-	HCl	35	40 Min.	Rückfluss-tempe-ratur	173	171

lieferte wiederum die entsprechenden Epoxy-Ketone nicht und die drei isomeren Nitro-phenacylbromide auch nicht.

Experimenteller Teil[1]

A) Die Darstellung von Nitro-hydroxy-phenacylbromiden

1. 2-*Nitro*-3-*hydroxy-phenacylbromid* 0,181 g (1 mMol) Keton wurde in 1—2 ml Eisessig gelöst, mit 0,05 ml (1 mMol) Brom versetzt und zunächst bis zur Entfärbung und dann noch weitere 5 Minuten über offener Flamme erwärmt. Nach dem Erkalten wurde die Lösung in 10 ml Eiswasser geschüttet, in dem sich ein gelber Niederschlag bildete. Umkristallisieren aus einem Tetrachlorkohlenstoff (Benzingemisch) (1:10).

2. 4-*Nitro*-3-*hydroxy-phenacylbromid* 0,181 g (1 mMol) Keton wurde im 2—3 ml Chloroform gelöst, mit 0,05 ml Brom versetzt, am Wasserbad bei cca 50° C bis zur Entfärbung erwärmt und noch weitere 10 Minuten bei dieser Temperatur gehalten. Nach Eindampfen in Luftstrom erfolgte Umkristallisieren aus einem Tetrachlorkohlenstoff (Benzingemisch) (1:10).

3. 6-*Nitro*-3-*hydroxy-phenacylbromid.* 0,181 g (mMol) Keton wurde in 50 ml, einem 1:1 Tetrachlorkohlenstoff (Chloroformgemisch gelöst, 0,05 ml (1 mMol) Brom zugegeben und nach eingetretener Entfärbung die Lösung über offener Flamme noch 5 Minuten erwärmt. Nach Verdampfen des Lösungsmittels an der Luft wurde ein Öl erhalten welches nach 24 Stdn, erstarrte. Umkristallisierung aus einen Tetrachlorkohlenstoff Benzingemisch (1:10).

B) Darstellung der Epoxyketone

1. *Darstellung in Gegenwart von Natriummethylat-Katalysator.* 0,260 g (1 mMol) Nitro-hydroxy-phenacylbromid und aequivalente Menge Benzaldehyd bzw. 4-Nitrobenzaldehyd wurde in 10 ml Methanol gelöst, mit 10 ml Katalysatorlösung (0,04 g Natrium in 10 ml Methanol gelöst) versetzt nach Ablauf der verschiedenen

[1] Die Schmelzpunkte sind unkorrigiert

Reaktionszeiten (Tab. IV., V.) das Gemisch in 40 ml Wasser geschüttet und mit 5 n Salzsäure angesäuert. Die Substanzen schieden gewöhnlich Kolloid aus, so daß es erts nach längerer Zeit filtriert wurde. Umkristallisieren aus einen Wasser-Acetongemisch (4:1).

2. *Darstellung in Gegenwart von Natriumhydroxid-Katalysator.* Mit den gleichen Mengen wie im Falle des Natriummethylat-Katalysators, aber es war die Katalysatorkonzentration (0,2 g Natronlauge in 10 ml Wasser) und *die Reaktionszeiten versehiedene* {[1] und Tab. IV.}.

3. *Darstellung in Gegenwart von Salzsäure-Katalysator. a) 1-(4-Nitro-phenyl)-2-(3-nitro-4-hydroxy-benzoyl)-aethylenoxyd.* 0,25 g (1 mMol) 3-Nitro-4-hydroxy-phenacylbromid und 0,151 g (1 mMol) 4-Nitro-benzaldehyd wurden in 20 ml, mit Salzsäure kalt gesättigten absoluten Aethanol gelöst und die Lösung nach 90-stündigen Stehen bei Raumtemperatur mit Natriumhydroxyd auf pH = 5 – 7 eingestellt. Nach Verdünnen mit 30 ml Wasser wurde eine schwach gelbliche Kolloid-Substanz erhalten, die nach längerem Stehen koagulierte. Umkristallisieren aus einem Aceton-Wassergemisch (1:4).

b) 1-(4-Nitro-phenyl)-2-(3-hydroxy-4-nitro-benzoyl)-aethylenoxyd

0,260 g (1 mMol) 3-Hydroxy-4-Nitro-phenacylbromid und 0,151 g (1 mMol) 4-Nitro-benzaldehyd werden in mit 5 ml Salzsäure gesättigem absoluten Aethanol 40 Minuten am Rückflußtemperatur erwärmt.

Die Reaktion lief mit geringer Ausbeute auch so als *a)* ab.

c) 1-(4-Nitro-phenyl)-2-(3-hydroxy-2-nitro-benzoyl)-aethylenoxyd

Die Reaktion zwischen, 0,26 g (1 mMol) 2-Nitro-3-hydroxy-phenacyl-bromid und aeqivalenten Mengen 4-Nitro-benzaldehyd spielte sich nur so als *b)* ab.

C) 2-(3-Nitro-4-hydroxy-phenyl)-3-(4-nitro-benzyl)-kinoxalin

0,018 g 4-Nitro-phenyl-3-nitro-4-hydroxy-benzyl-glyoxal wurde in einer Lösung aus 0,018 g Ortho-phenylen-diamin in 10 ml 95%-igem Aethanol suspendiert und das Gemisch eine Stunde lang gekocht. Nach Abfiltrieren der ungelöst gebliebenen Substanz treten im Kühlschrank gelbe Kristalle aus. Schm.: 219—220° C (Umkristallisiert in Aethanol.) Analyse: $C_{21}H_{14}N_4O_5$(402,3) Ber.: C 62,7 H 3,5 Gef.: C 62,8 H 3,6.

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О КОНДЕНСАЦИИ ДАРЗЕНСА НИТРО-ГИДРОКСИ-АЦЕТОФЕНОНОВ

Г. Шипош, Б. Цукор, И Добо

Была произведена конденсация Дарзенса несколькими нитро-гидрокси-фенацилбромидами. Произведение конденсации удалось и в присутствии катализатора соляной кислоты. Относительно получения фенацилбромидов были сделаны несколько наблюдений.

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